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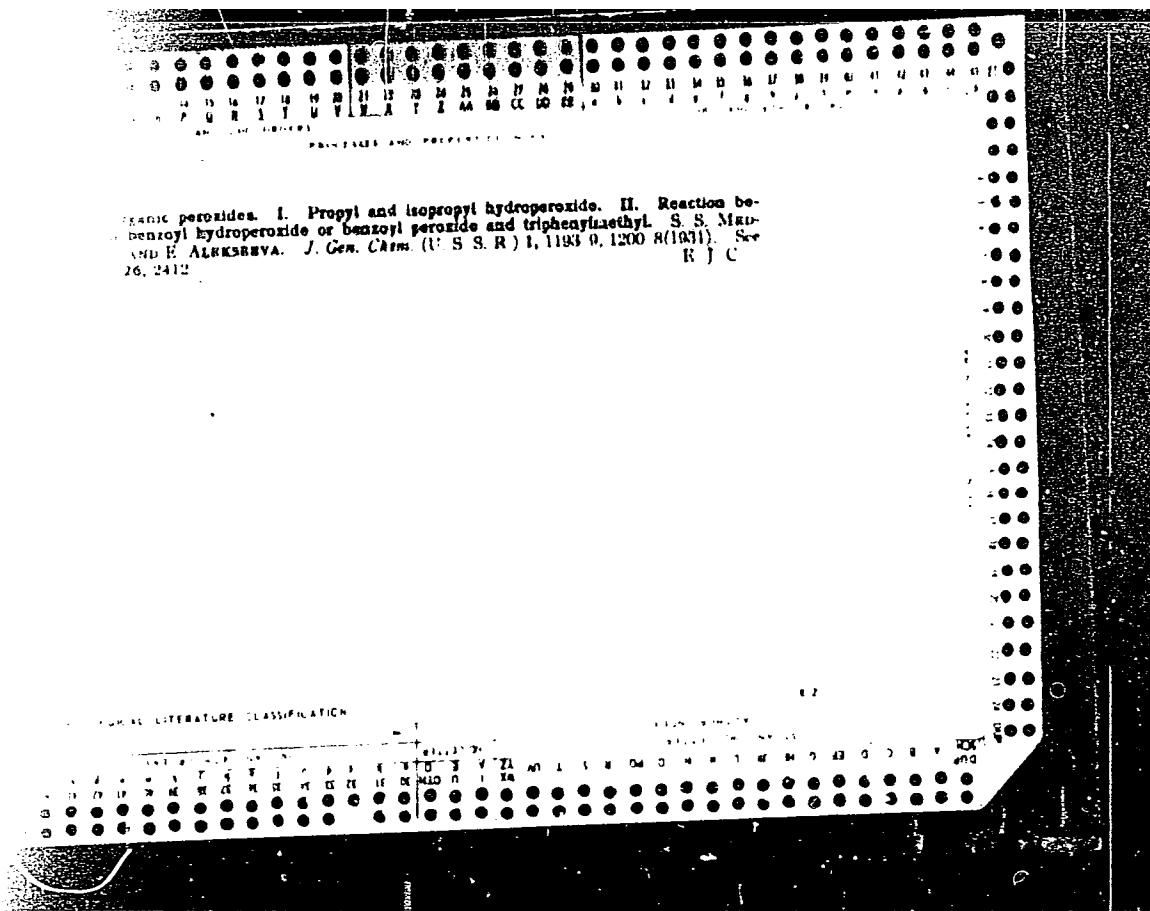
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CIA-RDP86-00513R001033310001-9"



Oxidation of methane to formaldehyde S. S. Medvedev. *Natural Gas U. S. S. R.* No. 4, 5, 29-32 (1932). CH<sub>4</sub> passed over a catalytic mass prepared from Fe borate and SiO<sub>2</sub> phosphate at 800-10° yielded 19.3 mg. of CH<sub>2</sub>O per l. of gas mixt. Presence of aqueous (0.3%) HCl in the gas mixt. considerably increased the yield of CH<sub>2</sub>O in the presence of Al and Fe phosphate catalysts, but on a further increase of the HCl concn. the yield was lowered. An increase in O<sub>2</sub> in the gas mixt. favored the formation of CH<sub>2</sub>O, but lowered the "useful oxidation" of H<sub>2</sub>. The oxidation of CH<sub>4</sub> with air (in the presence of catalysts) yielded 5% of CH<sub>2</sub>O; oxidation with O<sub>2</sub> yielded 3%. A change in the gas mixt. during the reaction had little influence on the yield and composition of the formalin condensate. The liquid condensate contained 25-40% HCHO. A layout of the app. for the oxidation of CH<sub>4</sub> from the Sverdlovskhany natural gas (CO<sub>2</sub> 20.5, O<sub>2</sub> 3.51, N<sub>2</sub> 19.0, CH<sub>4</sub> 55.9 and C<sub>2</sub>H<sub>6</sub> 3.04%) is given. A. Podgorny

Velocity of the reaction between organic per acids and cyclohexene. N. Medvedev and O. Blokh. *J. Phys. Chem.* U.S.S.R. 4, 725 (1930). -Studies of perbenzoic,  $p$ -methoxyperbenzoic,  $p$ - and  $m$ -nitroperbenzoic,  $p$ -nitro- $m$ -naphthoic, peracetic and phenylperacetic acids show that the reaction between org. peroxides and cyclohexene at 20° in the main follows the bimol. law (order as a const. of the 2nd order), is a function of the concentration of peroxide, but does not depend upon the concentration of cyclohexene. The nature of the solvent does not affect the speed of reaction of peroxide with cyclohexene greatly; the speed of reaction of peroxide with cyclohexene in benzene,  $x$ , in xylene,  $y$ , in acetone,  $z$ , in  $N$  in xylene being constant in the ratio  $x:y:z=1:1:1$ . The reactivities of acyl radicals in these peroxides are in the same order as for the corresponding acyl halides. The values of  $K$  at 26 ± 0.1° increase in the same order and are for the per acid in acetone at 26° and in xylene at 0° and 26°, resp., as follows: peracetic, 0.047, 0.072; perbenzoic 0.694, 0.695;  $p$ -nitrophenylperacetic, 0.103;  $p$ -methoxyperbenzoic, 0.050, 0.212;  $m$ -naphthoic, 0.877;  $p$ -nitro- $m$ -naphthoic, 0.540;  $p$ -nitro- $p$ -nitrophenylperacetic, 0.261;  $p$ -nitrophenylperbenzoic, 0.243.

210. The energy of activation is fairly const. and equal to 14,000 cal., while the Arrhenius coeff.  $\beta$  varies from  $2 \times 10^4$  for  $p$ -methoxybenzoic to  $4 \times 10^4$  for  $p$ -nitrobenzoic acid. P. H. R.

Hydrolysis of halo methanes A. D. Abkin and S. S.  
Medvedev Russ. 34, 551, Feb. 28, 1934 Halo-methanes  
are hydrolyzed at elevated temps. and in the vapor phase  
in the presence of catalyst of phosphates or borates of Sn,  
Tl, Zn or Pb, or their mixts. in substance or pptd. on cat  
thus

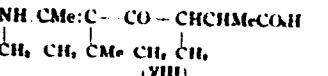
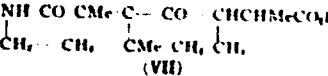
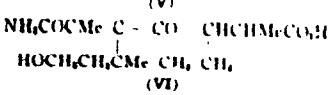
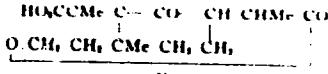
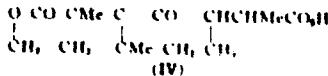
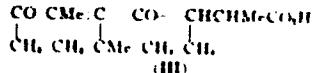
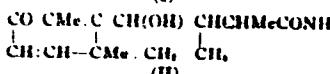
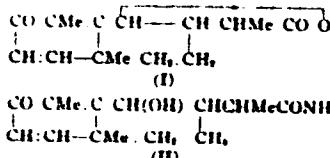
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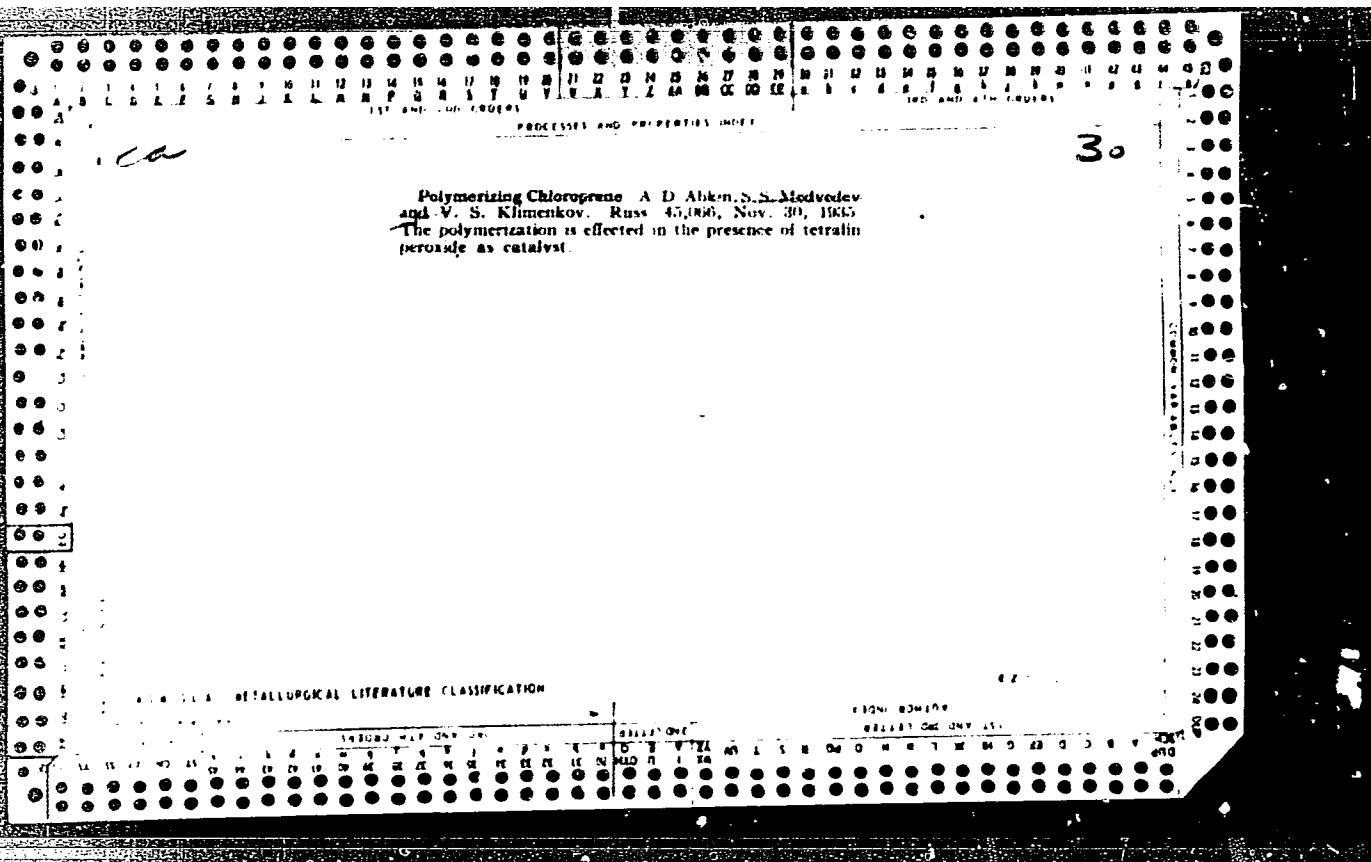
The vapor phase catalytic hydrolysis of alkyl halides.  
II. The preparation of methanol, formaldehydes and  
benzoyl chloride from methyl chloride, dichloromethane  
and benzotrifluoride. A. Abkin and S. Medvedev.  
*J. Chem. Ind. (Moscow)* 1934, No. 1, 30-4; cf. *J. Russ. Chem. Chem.* U. S. S. R., 6, 731 (1933). MeCl and CH<sub>2</sub>Cl<sub>2</sub>  
may be hydrolyzed by passing them with steam over Sn  
phosphate deposited on pumice. TiO<sub>2</sub> and mixts. of  
Sn and Fe phosphates are unsatisfactory. When hy-  
drolyzed at 400°, MeCl gives 10% MeOH and 18.6%  
CH<sub>2</sub>O. CH<sub>2</sub>Cl<sub>2</sub> gives 78.5% CH<sub>2</sub>O. If mixts. of MeCl  
and CH<sub>2</sub>Cl<sub>2</sub> are run at 400°, CH<sub>2</sub>Cl<sub>2</sub> gives 90% CH<sub>2</sub>O  
and the MeCl is 99% hydrolyzed. The residual MeCl  
may be recirculated, in which case 3-4 cycles are required  
for its complete hydrolysis, or it may be further chlorinated  
to CH<sub>2</sub>Cl<sub>2</sub>. The ratio of chlorides to H<sub>2</sub>O for hydrolysis  
should be 1:10. PhCCl<sub>3</sub> and H<sub>2</sub>O in the ratio 1:1 at  
400° give 98% H<sub>2</sub>O. H. M. Lester

ASA-SEA METALLURGICAL LITERATURE CLASSIFICATION

100% CROWN  
CLASSIFICATION  
EXEMPT FROM  
DISSEMINATION  
EXEMPT FROM  
REFORMATTING  
EXEMPT FROM  
REFILING  
EXEMPT FROM  
RESEARCH  
EXEMPT FROM  
STANDARDIZATION  
EXEMPT FROM  
TELETYPE  
EXEMPT FROM  
TRANSMISSION  
EXEMPT FROM  
TRANSLATION  
EXEMPT FROM  
TYPEWRITING

The structure of *santolin* and *santonic acid*. A. Abbie and S. Medvedley, *J. Gen. Chem. (U. S. S. R.)* 1407-14(1934).—Santonin (I) dissolved in liquid NH<sub>3</sub> in a sealed tube at room temp. within 3 days. Evapn. of the NH<sub>3</sub> and purification of the residue with dry boiling pH 7 gave in quant. yield the *amide* (III) of *santonic acid*, m. 102-3° (decopmp.). II with hot alkali soln. + alc. and H<sub>2</sub>O readily gave I, although dry II is stable. II crystal. from CHCl<sub>3</sub> with 1 mol. of CHCl<sub>3</sub> removed completely only by heating in vacuo. In the presence of moisture both NH<sub>3</sub> and CHCl<sub>3</sub> were evolved while the crystal form was retained. It was not possible to convert II to the lactam analog of I. Addnl. evidence was obtained for the structure III for *santonic acid*. An improved method for prep. III consists in refluxing 250 g. Na(OH)<sub>2</sub> with 250 cc. H<sub>2</sub>O for 1 hr. in the absence of CO<sub>2</sub>, then adding 50 g. of I and boiling for 12 hrs. Cooling, shaking in portions with concd. HCl, extg. with Et<sub>2</sub>O, evapn. the Et<sub>2</sub>O, purifying by dissolving in Na<sub>2</sub>CO<sub>3</sub> soln. and reppig. with HCl, and finally recryst. twice from 60% alc. gave colorless III, m. 102-3°, in 55% yield. III with H<sub>2</sub>SO<sub>4</sub> gave a lactone (IV), which could be converted to another lactone (V). IV gave the amide (VI) with liquid NH<sub>3</sub>. VI gave the lactam (VII) but could not be converted to VIII. III (15 g.) in 200 cc. AcOH





Thermal decomposition of methyl hydrogens peroxide. S. Medvedev and A. Podyapol'skaya. *Acta Physicochim. U.R.S.S.*, S. 2, 497-504 (1935) (in German).—A stream of pure N<sub>2</sub> was passed through MeCOOH, in glass heated to 200-300°. The products of reaction are MeOH, MeO, HCHO, HCO<sub>2</sub>H, O<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O but no H<sub>2</sub> or CH<sub>4</sub>. MeOH was detd. by reaction with 1 cc. 25% H<sub>2</sub>SO<sub>4</sub> and 1.5 cc. 10% KI, left standing for 1 hr. and then titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln. The value so found is then 78.9%, 80.2% and 90.8% of the true content of MeOH for 0.2, 0.1 and 0.05 cc. solns., resp. (cf. Riccini and Hitz, *C. A.*, 24, 1078). HCHO was detd. iodometrically in alkali. A correction for MeOOH was made. HCO<sub>2</sub>H was converted to the Na salt, and then detd. by the KMnO<sub>4</sub>-KI-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> method, and a 4% correction factor applied. Cases were detd. in a Schmidt app. The C-H balance was always good for the sum of the products. The compn. of the products of the reaction

for various times of contact at temps. from  $20^{\circ}$  to  $300^{\circ}$  indicates that the amt. of MeOH rises to 62% then slowly falls to 40% and less, CO rises to 23%, MeO very slowly rises to at least 25%, HCHO rises to 10%, HCOOH to 5% and  $\text{CO}_2$  appears late, rises to 5% and then slowly decreases again. The sum of MeOH and MeO after the max. of MeOH is const. With increasing temp. of decompp., the amt. of MeO increases and MeOH decreases but the sum increases;  $\text{O}_2$  increases, HCOOH decreases to 5%, CO is const.,  $\text{CO}_2$  increases. These results indicate 2 processes, viz.  $\text{MeOOH} = \text{CH}_3\text{OH} + \text{H}_2\text{O}$ ,  $\text{MeOOH} + \text{ECHO} = \text{MeOOCCHOH} = \text{HCOOH} +$

$\text{H}_2\text{O}$ ,  $\text{MeOH}$  +  $\text{HCO}_2\text{H}$

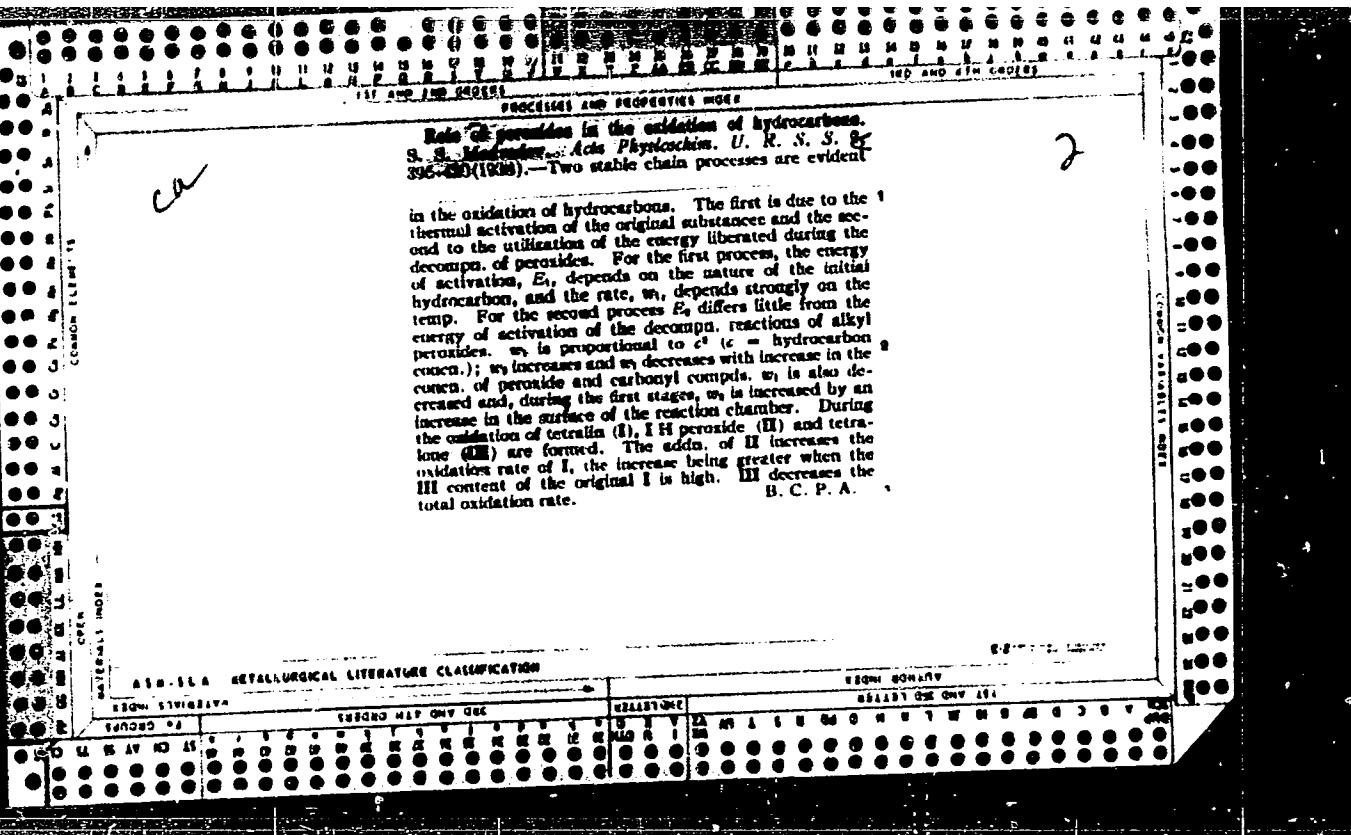
$\text{MeOH}_2$  and  $\text{HCO}_2\text{H} \rightarrow \text{CO} + \text{H}_2\text{O}$  with an over-all activation energy of 10,950 cal. and  $k_1 = 0.0108$  at  $200^\circ$ ,  $0.0012$  at  $300^\circ$  and  $2\text{MeOH} \rightarrow \text{MeOH} + \text{O}_2$ ,  $2\text{MeOH} \rightarrow \text{MeO} + \text{H}_2\text{O}$ ,  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ , with  $E = 25,330$  cal. and  $k_2 = 7.00$  at  $200^\circ$  and  $812$  at  $300^\circ$ . F. H. R.

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Kinetics and mechanisms of organic polymerization  
processes. S. S. Melvilley, *Ind. Chem. Ind.* (U. S.  
& R.) 2, 472 (1971). A discussion based chiefly on  
literature with 20 references. Chas. Illam

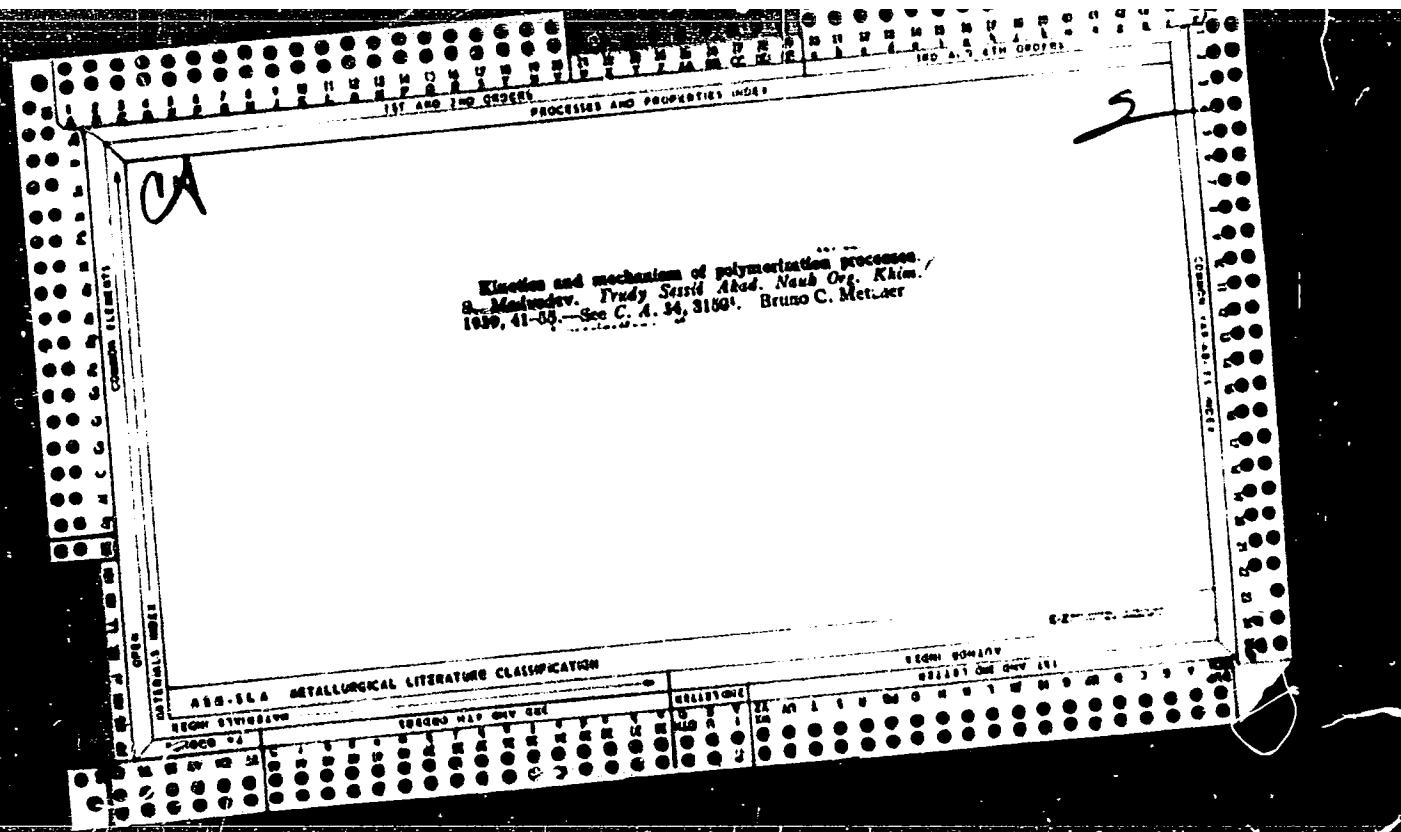


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CA  
New debarking machine at the Balakhninskii paper mill.  
E. V. Khovanskii and N. S. Afanasyev. *Бумажная промышленность*,  
from, 16, No. 7, 67-73 (1981). Performance of the BTS  
debarking machine. B. I. Zalegalier. *Ibid.* 74-7.  
Knives of the BTS debarking machine. B. V. Zoteva.  
*Ibid.* 78-80. -Construction and operation details.

Chas. Blanc

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The polymerization of chloroprene. I. Influence of tetrahydroperoxide on the kinetics of the polymerization of chloroprene in the condensed phase. B. Medvedev, K. Chilikina and V. Klimenkov. *Acta Physicochim. U. R. S. S.*, 11, 751-69 (1939) (in Russian).—Exptl. data on the rate, extent and course of the product of polymerization at 20-80° with 0-5% hydroperoxide added are given. The total amt. of polymerized chloroprene is given by  $s = \left( \frac{A_1 C}{A_1 C + A_2} \right) K^{1/(n-1)}$ , where  $K$  is the const. for the thermal, uncatalyzed reaction;  $A_1$  for linear and  $A_2$  for lateral polymerization.  $C$  is the concn. of tetrahydroperoxide. Addn. of tetrahydroperoxide increases only the rate of linear polymerization. The activation energies  $e_a$ ,  $e_m$ ,  $e_l$  and the reaction consts.  $k$ ,  $k_m$ ,  $k_l$  at 30° are 20.2, 10.5, 20.2 Cal., and 0.03, 0.17, 0.017, resp. The reaction is autocatalytic. The side-chain process can set in only after linear polymerization (thermal or catalytic) has already begun and amounts to a rupture of the chain reaction of the activated linear process. The linear, elastic  $\mu$  form remains only when polymerization is far progressed, and it due to a considerable development of the side-chain process, at the same time leading to an increased rate of reaction. F. H. R.

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PART II

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600

MEDVEDEV4S8

1. MELVEDEV, S.; CHILIKINA, Ye.; KLIMENKOV, V.

2. USSR (60C)

"The Polymerization of Chlorophrene" Part I. "The Kinetics of the Polymerization of Chlorophrene in the Condensed Phase Under the Influence of Hydrogen Peroxide of Tetralin," Zhur. Fiz. Khim., 13, No. 9, 1939. Moscow, Physico-Chemical Institute imeni Karpov, Laboratory of Polymerization Processes. Received 21 April 1939.

Report U-1615, 3 Jan. 1952.

MEDVEDEV4S8

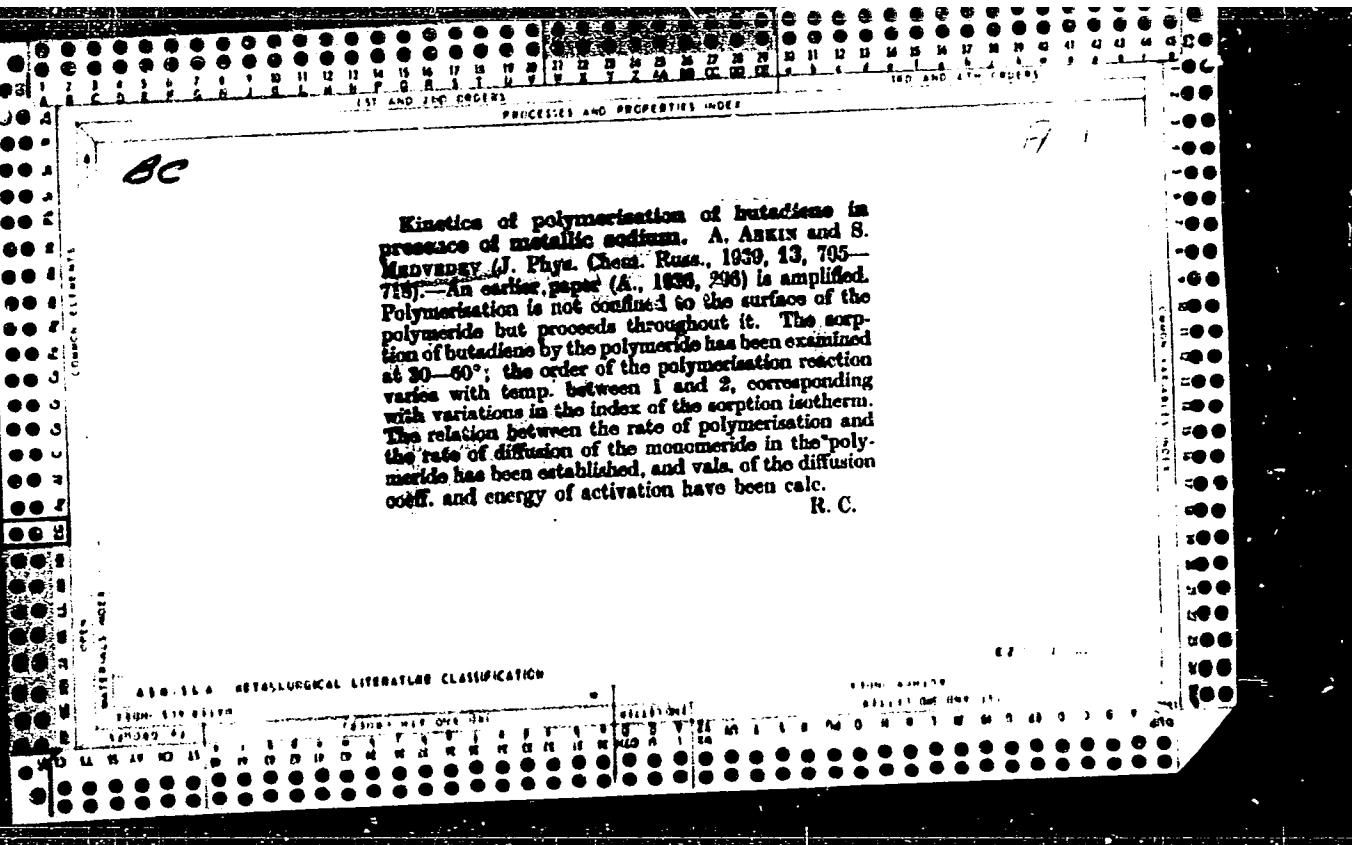
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1. CHILIKINA, Ye.; MEDVEDEV, S.

2. USSR (600)

"The Joint Action of Hydrogen Peroxide of Tetralin and Nitro Compound on the Polymerization of Chlorophrene" Part II, Zhur. Fiz. Khim., 13, No. 9, 1939.  
Moscow, Physico-Chemical Institute imeni Karpov, Laboratory of Polymerization Processes. Received 21 April 1939.

Report U-1615, 3 Jan. 1952



Oxidation of tetrahydronaphthalene in condensed phase. S. MARENKOVA and A. PODJAPOLSKAJA (J. Phys. Chem. Russ., 1939, 13, 719-737; cf. A., 1939, I, 148).—Oxidation by  $O_2$  at 65-85° yields chiefly tetralin H peroxide (I) and tetralone (II); no acids or aldehydes are formed. (I) accelerates the reaction, whilst (II), which is formed by the decomp. of (I), retards, by an amount which rises and then becomes const. as the concn. of (II) increases. The oxidation can be resolved into two independent stationary chain reactions. One arises from the thermal activation of tetralin, is retarded by (II), and proceeds by a mechanism similar to that of the oxidation of MeCHO (A., 1931, 372), and the second depends on the decomp. of a compound formed on the wall by collision of a (I) mol. with an adsorbed (II) mol., and is accelerated by (II). Both reactions lead to the accumulation in the system of (I), which gives the oxidation an autocatalytic character.

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MEDVEDEV S.S.

1ST AND 2ND CLOTHES

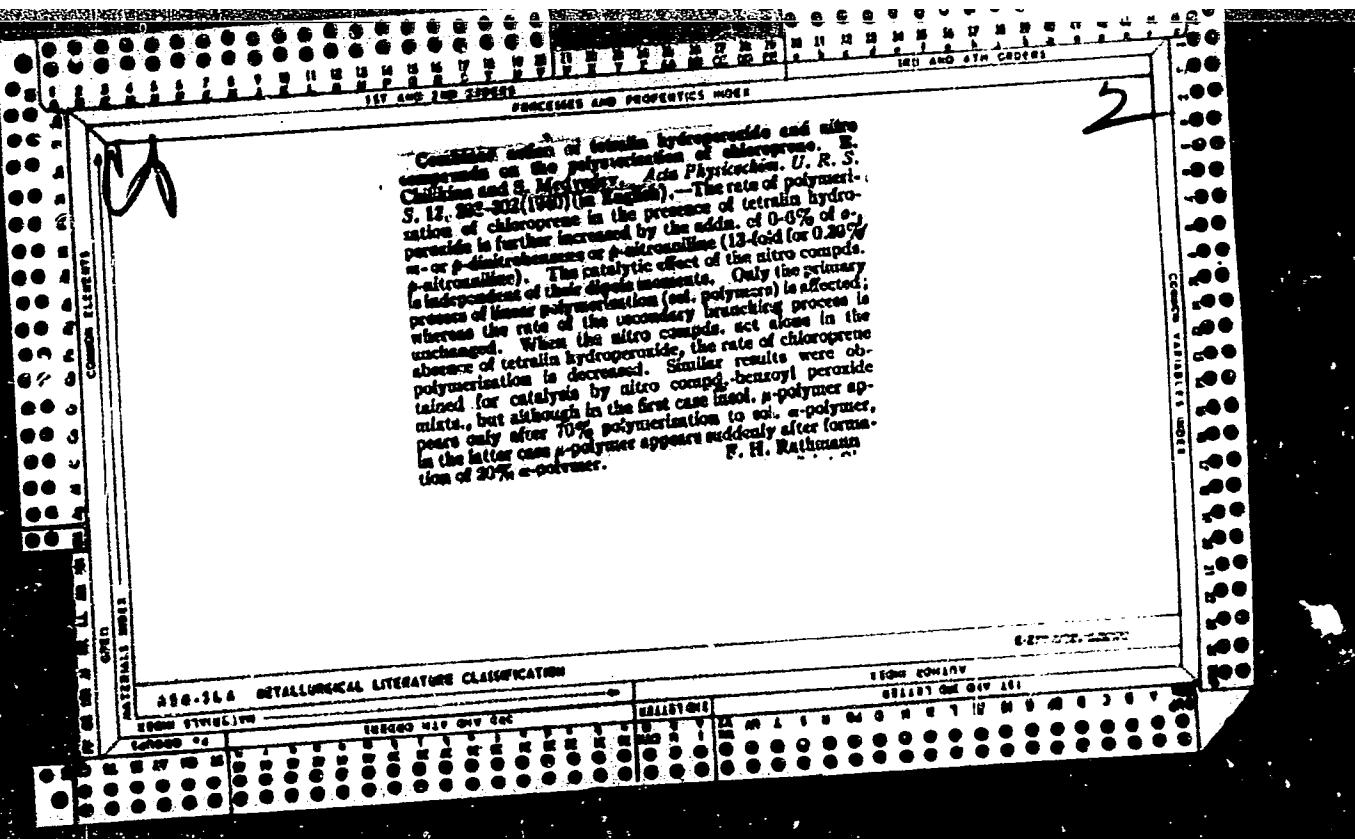
ANSWER AND EXPLANATION PAGE

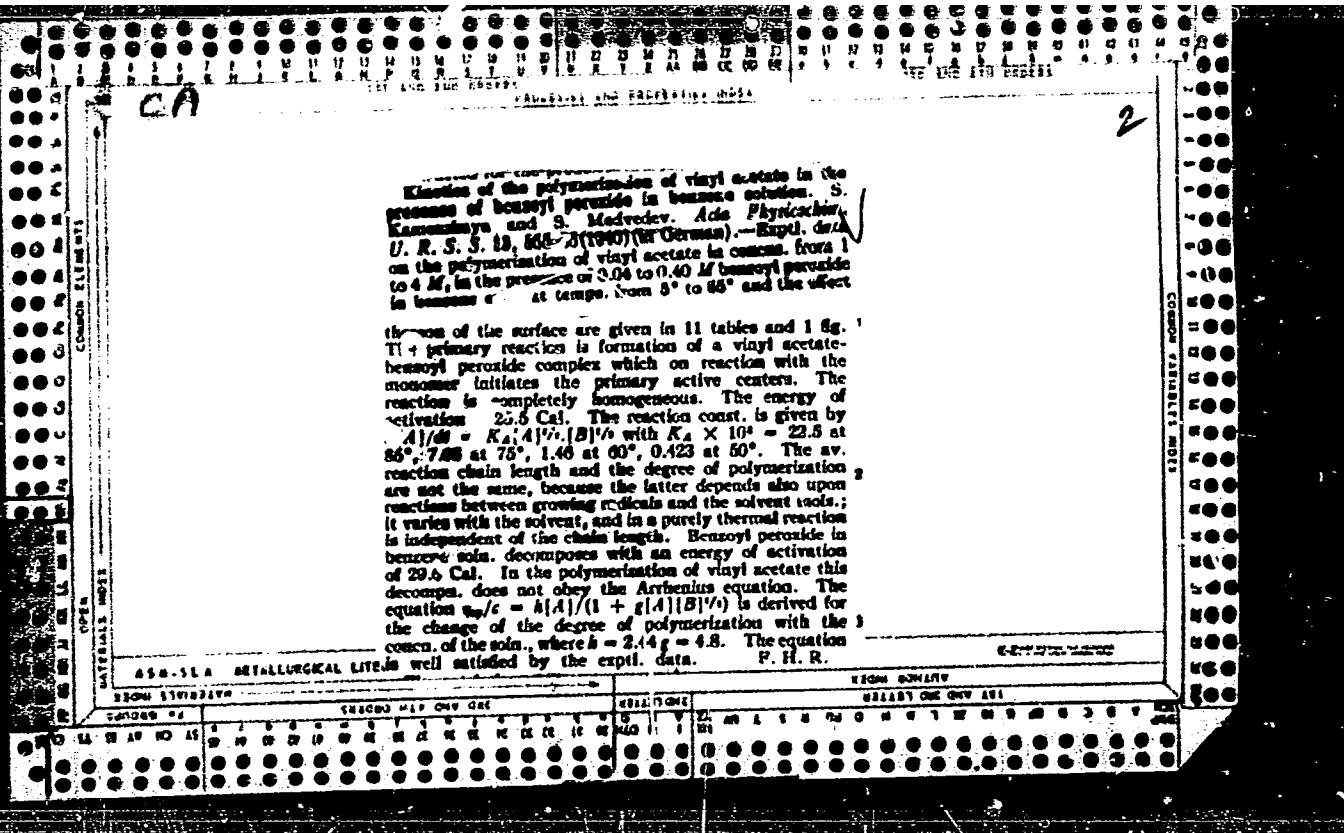
102 AND 111 CROSSES

Kinetics of the polymerization of 2-chloro-1,3-butadiene catalyzed by benzoyl peroxide in dibutyl phthalate solutions. S. S. Medvedev, L. Glidin and M. Lazareva. *J. Phys. Chem. (U. S. S. R.)* 13, 1392-1402 (1939).—The kinetics of the polymerization of chloroprene (I) and the distribution of I in the gas and liquid phases were detd.

by a manometric method. The solv. of I in dibutyl phthalate is given by  $P/C^2 = K$  with  $\epsilon = 0.730$ ,  $K = 2.15$  at  $30^\circ$ ;  $\epsilon = 0.822$ ,  $K = 3.93$  at  $60^\circ$ . The polymerization process is heterogeneous; the rate increases with increasing concn. of I and benzoyl peroxide (III) only up to a certain max. and then remains const. This max. is greater the greater the surface available, varying from 2 to 8% II. With 4% II, the energy of activation between  $30$  and  $60^\circ$  is 12.5 Cal. On the basis of an analysis of the kinetic data, it is concluded that the initial active centers form as the result of reaction between I and ionized II radicals adsorbed on the walls. These reaction nuclei then leave the wall and the polymerization process takes place in the soln. vol. Deactivation may occur either by reaction with un-ionized II or by collision with adsorbed molcs. of I.

E. H. Rathmann





MAMONTOVA, O.: ABBIN, A.: MEDVEDEV, S.

Polymerization Processes Laboratory, Moscow Physico-Chemical Institute im. L. Ya. Karpov,  
(-1939-)

"The Kinetics of Polymerization of Butadiene - 1,3 in the Presence of Potassium  
Phenylisopropyl (Fenilizopropilkaliya)."

Zhur. Fiz. Khim., Vol. 14, No 1, 1940.

KALENSKAYA, S.; MEN'KOV, S.

Moscow

La oratory of Polymerization Processes, Physico-Chemical Institute named L.  
Yu. Karpov, (-1944-).

"The Kinetics of Polymerization of Vinyl Acetate in the Presence of  
Benzoyl Peroxide in a Benzene Solution."

Zhur. fiz. khim., vol. 14, No. 1, 1940.

A. J. E. W.

Changes in Raman spectra of chloroprene and isoprene in the polymerisation process. A. Gantcharov and S. Medvedev (et al.)  
Physikokhim. U.R.S.S., 1948, 10, 1-11).—Raman data are given for chloroprene (I), a 30% solution of polymerised (II) in the monomeride, a solution of the polymeride in  $C_6H_6$  or  $CCl_4$ , and the pure polymeride; corresponding data are also given for isoprene (III). In each case polymerisation gives rise to a non-conjugate double bond line [1660  $\text{cm}^{-1}$  in (I) and 1663  $\text{cm}^{-1}$  in (III)] not given by the monomeride; a conjugate double-bond line (1630, 1640  $\text{cm}^{-1}$ ) decreases in intensity as polymerisation proceeds, but remains much stronger than the 1660-1663  $\text{cm}^{-1}$  line when ~30% of polymeride is present. The 1020  $\text{cm}^{-1}$  C-H line given by (I) is displaced to 1003  $\text{cm}^{-1}$  on polymerisation, and its intensity increases considerably. Changes in C-C and C-Cl lines are discussed. Polymerisation does not increase the background intensity of the spectograms  
A. J. E. W.

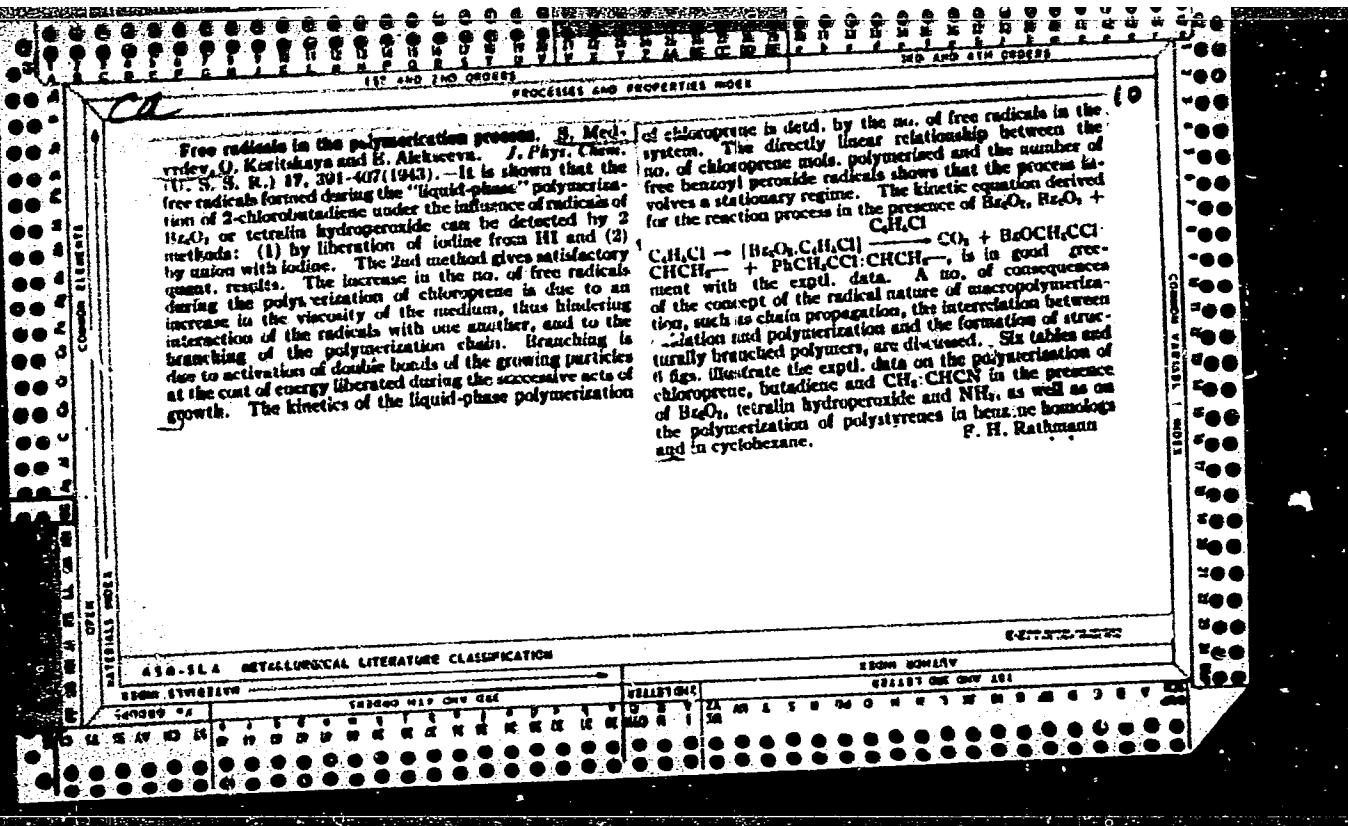
Karpov Inst.-Phys. Chem., Moscow

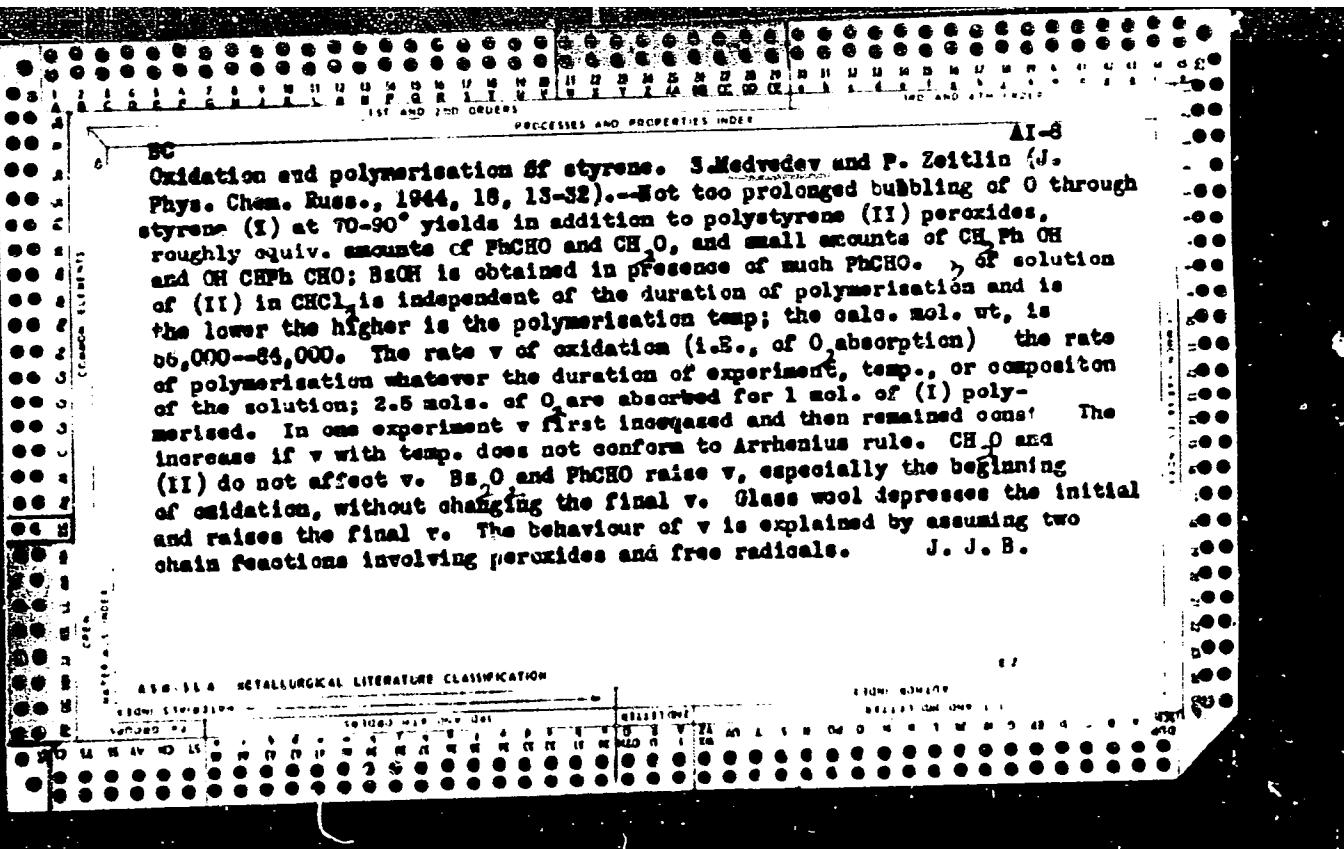
GAI TWAHER, A. R.; MEDVEDEV, S. S.

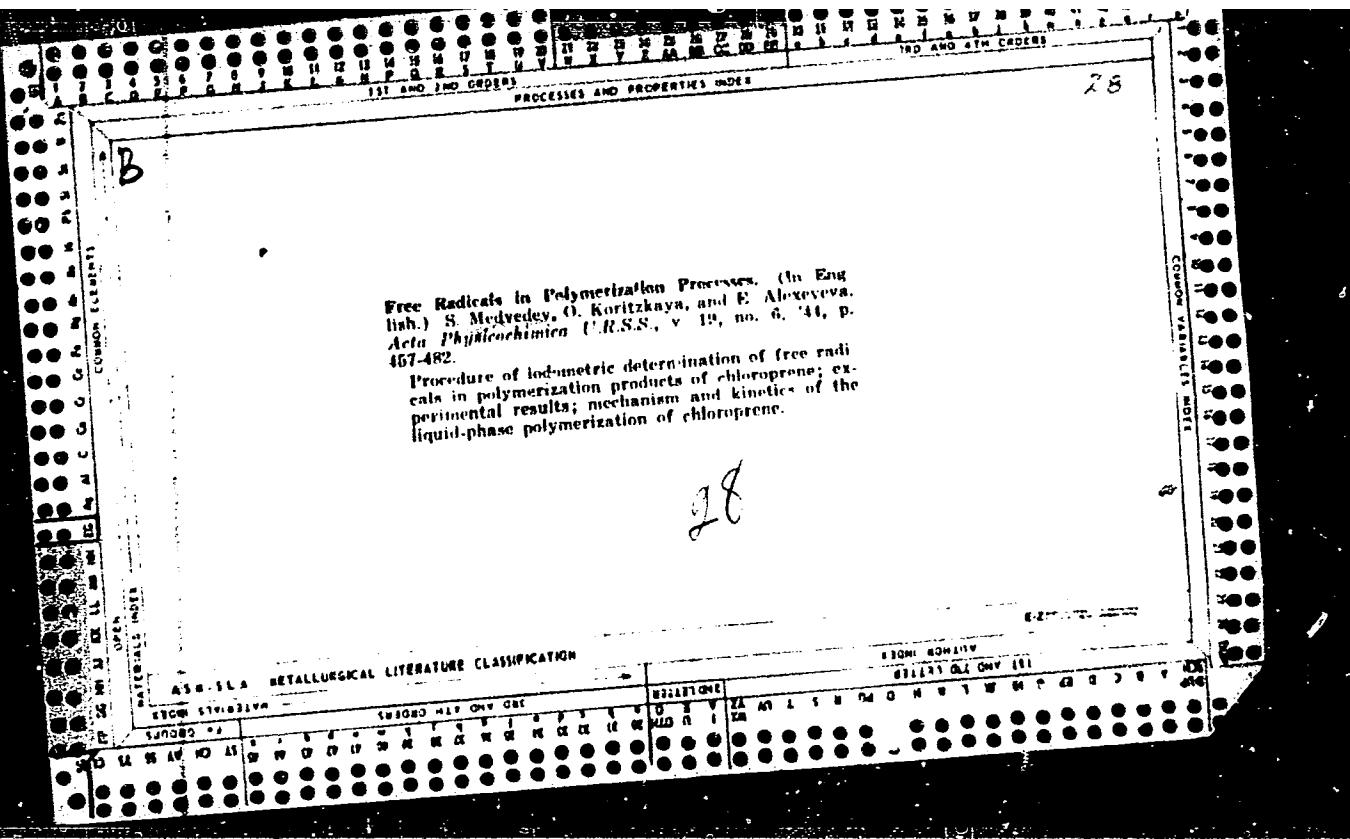
Physico-Chemical Institute imeni L. Ya. Karpov, Moscow (-1941-)

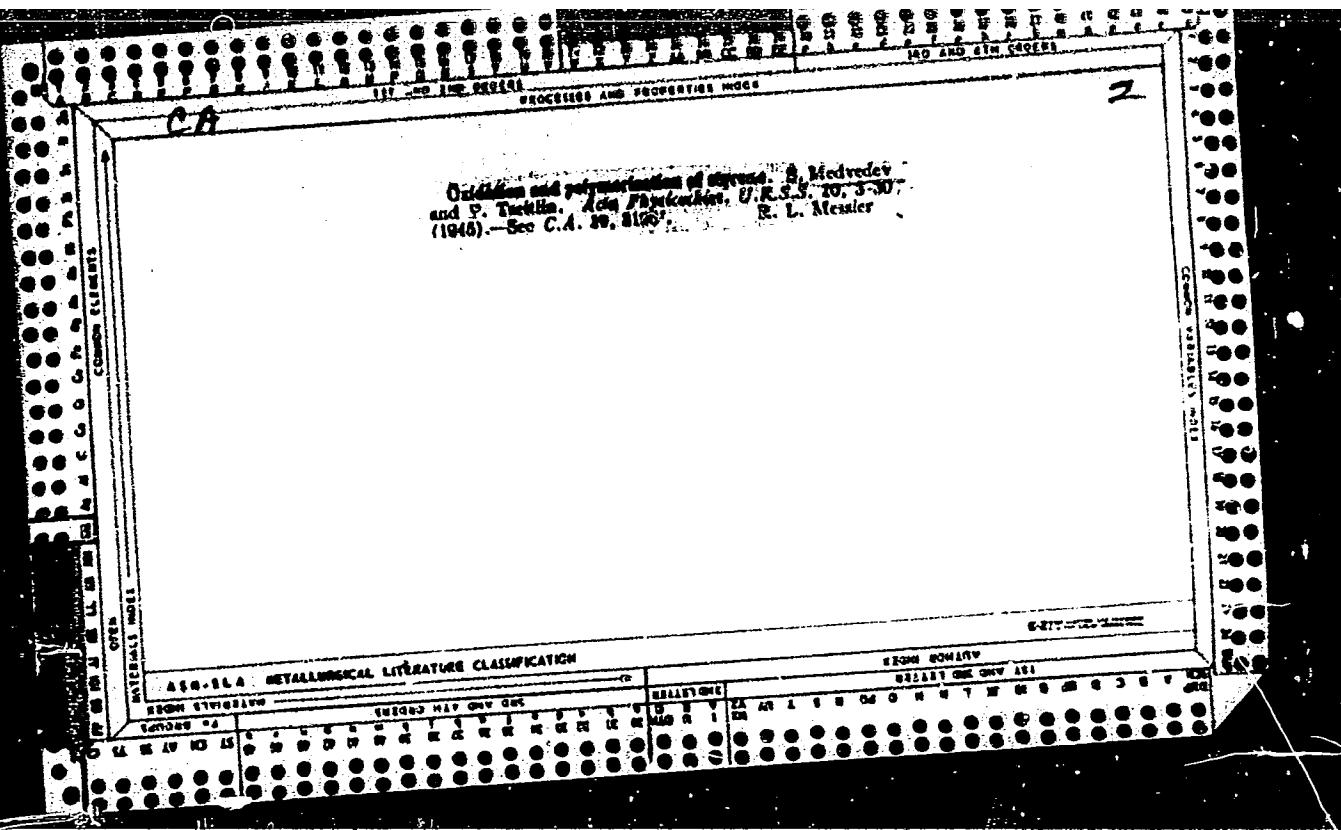
"The Change of the Raman Spectrum of Chloroprene and Isotrene in the Polymerization Process." Zhur. Fiz. Khim. Vol 17, No 1, 1943

BR-52050019









MEDVEDEV, S. S.

Kinetics of polymerization of hydrocarbons with a conjugated bond. P. S. Shantarovich and S. S. Medvedev  
(Inst. Chem. Phys., Acad. Sci. U.S.S.R., Moscow). J. Phys. Chem. (U.S.S.R.) 21, 1163-70 (1947) (in Russian). — 2-Chloro-1,3-butadiene was irradiated with 3030-3130  $\mu$ A., at the rate  $v$  of its polymerization declined from the vol. contraction. The  $v$  first rapidly increases, is then (e.g., for 8 hrs.) const., and increases again; the 2nd increase is associated with formation of a dense film at the irradiated wall. When the irradiation is continued for 5 or more hrs. and then stopped, polymerization goes on. Its  $v$  first decreases, then gradually increases, and starts to increase rapidly when 10% of the original chloroprene is polymerized. The  $v$  is greater the longer the preceding irradiation time, but the sharp rise of  $v$  occurs always at 10% transformation. The  $\omega$  polymer is the final product. When the irradiation time is 2 hrs., the rise of  $v$  at 10% transformation is less steep, and the  $\alpha$  polymer is the final product. When the  $\mu$  polymer forms, polymer chains grow and join to produce a net, and formation of links between chains in this net leads to the  $\omega$  polymer. The kinetics of these processes is cited, and is shown to agree with the

exptl. data. Irradiation of the com. polychloroprene (which is a mixt. of  $\alpha$  and  $\mu$  forms) sepd. from the monomer has no effect, but polychloroprene soaked in monomer is transformed into  $\omega$  polymer by light. The  $\mu$  polymer introduced into monomer causes polymerization of the latter to the  $\mu$  form, and this polymerization continues also when chloroprene which was in contact with  $\mu$  is run off the polymer. On the contrary, chloroprene induced to polymerize (to  $\omega$ ) by introduction of some  $\alpha$  ceases to polymerize when sepd. from the polymer. Polymers can be kept in a vacuum for months without losing their ability of inducing further polymerization. L. J. P.

**MEDEVDEV, S.**

The mechanism of the simultaneous polymerization of butadiene with vinyl cyanide and 1-methylvinyl cyanide under the action of benzoyl peroxide. I. Gindin, A. Abkin, and S. Medvedev (Karpov Inst. Phys. Chem., Moscow). J. Russ. Chem. (U.S.S.R.) 11, 1209-31 (1947) (in Russian). Mixts. of butadiene (I) ( $x$  wt. %) with CH<sub>2</sub>CN (II) (100 -  $x$  %) or CH<sub>2</sub>CMeCN (III) (100 -  $x$  %) and (BzO)<sub>2</sub> ( $y$  %) were prep'd. In N<sub>2</sub>, distd. (100 -  $x$  %) and (BzO)<sub>2</sub> ( $y$  %) were prep'd. In N<sub>2</sub>, distd. hrs., and distd. at room temp., in a high vacuum 20 hrs. The distn. residue (= polymer) was analyzed for N (i.e. the active C) and active O (i.e. BzO<sub>2</sub>). For the detn. of active nitrile and active O the polymer must be dissolved in CHCl<sub>3</sub>, not in acetone. The polymer must be dissolved in CHCl<sub>3</sub>, not in acetone. The rate  $v$  of formation of polymer decreases when  $x$  in. increases; e.g. at 60° for the system I + II ( $y$  being 0.6%) the initial rate is 0.26% per hr. at  $x = 0\%$  and 8.4% per hr. at  $x = 20\%$ . During one expt.  $v$  is almost const. at small  $x$  and increases with time at large  $x$ . The  $v$  increases with temp.; e.g. 42% polymer is attained at 60° within 63 hrs. and at 70° within 11 hrs. The  $v$  is proportional to  $\sqrt{y}$  between  $y = 0.3$  and  $y = 10$  wt. %. These results are discussed from the viewpoint of Abkin and Medvedev, C.A. 34, 7709. The polymerization ceases when one of the components is used up. The highest yield of polymer

(over 98%) is observed at  $x \approx 60\%$  for the I + II and near  $x = 70\%$  for the I + III system. The compn. of the polymer depends little on the time of polymerization and temp., but varies according to  $x$ . In the I + II system, the polymer contains more I than the original mixt. at  $x < 53\%$  and less than the original mixt. at  $x > 53\%$ . In the I + III system, the "acrotropic" mixt. has  $x \approx 60\%$ . The concn. of (BzO)<sub>2</sub> in the polymer decreases when  $y$  increases. However, polymerization continues also after (BzO)<sub>2</sub> concn. becomes zero. Monomer, distd. from the polymer and again mixed with it, polymerizes at the same  $v$  as if no distn. occurred, but soln. and reppin. of polymer remove its catalytic activity. The compn. of a copolymer depends on the consts.  $\alpha$  and  $\beta$  expressing the relative rates of reaction of 2 free radicals with the 2 components of the monomeric mixt. A simple method for computing  $\alpha$  and  $\beta$  from exptl. data is shown. From the values for  $\alpha$  and  $\beta$  the distribution of monomer groups within the copolymer can be calcd. (cf. C.A. 44, 403b). In the copolymer I + II, 67% II is present as one nitrile group between 2 butadiene groups; and in I + III 80% III is in this alternate pattern. The cessation of polymerization when 1 of the components is used up shows that both components are needed for the branching of the reaction chain.

J. J. Bikerman

"APPROVED FOR RELEASE: 07/12/2001

CIA-RDP86-00513R001033310001-9

GINDIN, L. M., ABRIN, A. D., and BEDVEDEW, S. S.

"Problems in Binary Co-Polymerization I. "Azeotropic" Mixtures," Dok. AN, 56, No. 2,  
1947

APPROVED FOR RELEASE: 07/12/2001

CIA-RDP86-00513R001033310001-9"

MEDVEDEV, S.

P. Khomikovskii and S. Medvedev, The mechanism of emulsion polymerization. I. The polymerization of vinyl cyanide in water solutions. P. 1027.

The problem of this work is the investigation of polymerization in water solutions, in solutions of emulsifiers (in the region of colloid solubility) and in emulsions in order to clear up the role of the processes going on in the separate parts of the emulsion system in the general process of emulsion polymerization. Vinyl cyanide, a monomer, was studied first because it is easily soluble in water. Potassium persulfate served as initiator of the polymerization.

The Karpov Physical Chemical Inst.  
Laboratory of Polymerization Processes,  
Moscow  
January 9, 1948

SO: Journal of Physical Chemistry (USSR) 22, No. 9, 1948

MEDVEDEV, S. S.

24213 MEDVEDEV, S. S. Vakuumirovaniye betona pristroitel'stvo tsemento-betonnykh dorozhnykh pokrytiy. Sbornik dokladov studentov Mosk. avtomob.-dor. IN-TA na 2-Y Nauch. konf-tsii studentov vyssh. Ucheb. zavedeniy S. Moskvy. ..., 1949, s. 37-42.

SO: Letopis, No. 32, 1949.

MEDVEDEV, S. S.

Khomikovskiy, P. M., Zabolotskaya, Ye. V. and Medvedev, S. S.  
"The polymerization of vinyl cyanide and methyl metacrylate  
in soap solutions and emulsions," In the symposium:  
Investigations in the field of complex-molecular compounds,  
Moscow-Leningrad, 1949, P. 45-55, - Bibliog: 6 items

SO:U-5241, 17 December 1953, (Letopis' Zhurnal 'nykh Statey, No. 2'. 1/49)

*Medvedev SS*

Catalytic polymerization of unsaturated compounds. Catalytic polymerization of styrene. A. R. Gantmakher and S. S. Medvedev. *Izdatelstvo Vsesoyuznoi Promstroit. Doklady & o Konf. Vysokomolekul. Soedinenii. Akad. Nauk S.S.R.* [1949, no. 63; cf. *CA*, 43, 7205; 47, 815].—Dilatometric and viscometric study of polymerization of  $\text{PhCH}_2\text{C}_6\text{H}_5$  was made at  $0^\circ$ ,  $10^\circ$ ,  $20^\circ$ , and  $30^\circ$  in  $\text{HCl}$  soln. with  $\text{CuCl}$  as catalyst. The rate is well defined by the equation:  $-dA/dt = K_1 K_2 [B]_0 [A]^2 / (K_3 + K_4 [A])$ , where  $[B]$  is initial catalyst concn.,  $K_1$  is the rate const. of initiation of chains (about  $2.002 \times 10^{-3}$  mole/l. min.),  $K_2$  is chain growth rate const. ( $1.8 \times 10^{-3}$  mole/l. min.),  $K_3$  is chain rupture rate const. ( $1.016 \times 10^{-4}$  mole $^{-1}$  min. $^{-1}$ ). This is derived on the assumption that catalyst units remain bound to the growing chain. In this process the recombination mechanism of chain rupture is absent. Characteristic viscosity is proportional to the square root of initial concn. of monomer and changes from 2.75 at  $0^\circ$  to 1.5 at  $30^\circ$ .  $\text{HCl}$  and  $\text{H}_2\text{O}$  accelerate the reaction; the former also accelerates chain rupture. At high concn. of monomer there will be observed an acceleration of the polymerization rate as the process proceeds; this is attributed to branched chain mechanism and is absent in peroxide-catalyzed reactions.

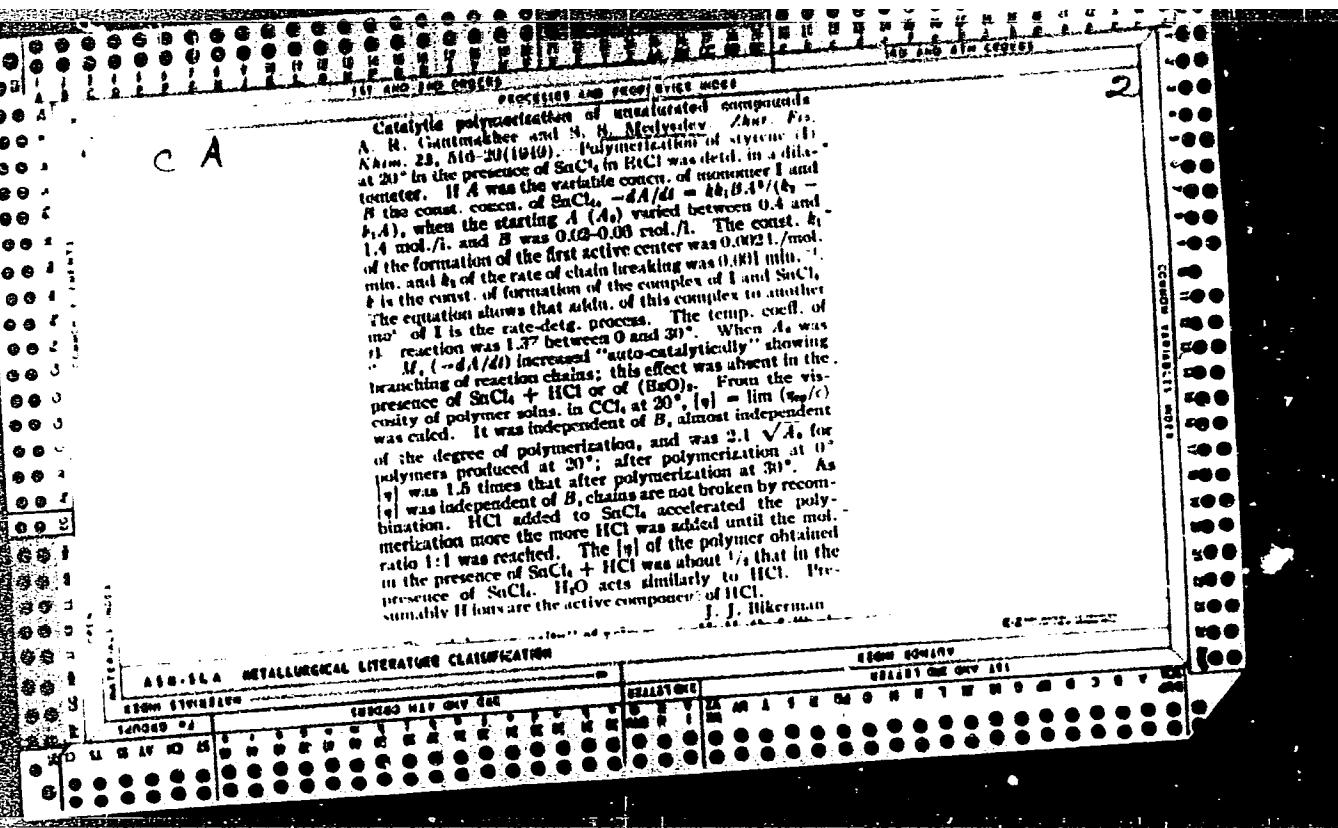
G. M. Kosolapoff

10

CH

Polymerization of allyl acrylate. I. Determining the structure and molecular weight of soluble forms of polyallyl acrylate. L. Gindin, S. Medvedev, and E. Flesher. *J. Gen. Chem. (U.S.S.R.)* 19, No. 3, 4127-35 (1949) (English translation). —See C.A. 44, 1024n. B. J. C.

Polymerization of allyl acrylate. I. Determination of the structure and molecular weight of the soluble forms of polyallyl acrylate. I. Gindin, S. Medvedev, and B. Flechler. *Zhur. Obshch. Khim.* (J. Gen. Chem.) 19, 1094-1701 (1949). Polymerization of allyl acrylate, b.p. 119.5-21.5°, n<sub>D</sub><sup>20</sup> 1.4330, d<sub>20</sub><sup>20</sup> 0.888 (2), in 2.0 and 5.7% solns. in C<sub>6</sub>H<sub>6</sub> with 1% Ba(OH)<sub>2</sub> catalyst at 60° gives low-mol. products, sol. in org. solvents, with the main chain linkage formed substantially from the "acrylic" double bond. The process followed dilatometrically to 80% polymerization, gave 35.0% total unsatn. of the product, which was almost identical with the "allyl" unsatn. (by the bromide-bromate method in CCl<sub>4</sub>, AcOH), the total unsatn. was detd. by the bromide-bromate method in the presence of HgSO<sub>4</sub>; the procedures were successfully tested on the monomer. G. M. Kosul'yanoff



CA

Rheotest of the single vinyl polymerization. I. Polymerization of vinyl acetate. V. B. Gantman and A. N. Medvedev. (Kazan Inst. Phys. Chem. Moscow) Zhur. Fiz. Khim. 25, 1626-41 (1951); cf. C.A. 45, 3008a. When  $\text{Cl}_2\text{C}_2\text{O}_4$  (I) was irradiated to remove the inhibitor present, its further polymerization in ultraviolet occurred without any induction period; hence, contrary to Cuthbertson, et al. (C.A. 33, 49619), the induction period was due to impurities. In the radiation of 3130-3130 Å, the rate of polymerization  $v$  (dose, millimoles/literally) was const. during an expt. for at least 90 min. In I solns. in  $\text{EtOAc}$ ,  $v$  was proportional to the mole fraction  $x$  of I between 0.02 and 1.00. After the irradiation was interrupted,  $v$  decreased in 100 sec. to 0.04 of its value. For pure I,  $v$  at 60° was 4 times that at 10°; hence, the energy of activation was 5000 cal. The ratio  $v_1/v_2$  of polymerization of I induced by  $(\text{HgO})_n$  is, according to the literature, proportional to  $n^{1/4}(%)$ , where  $n$  = concn. of  $(\text{HgO})_n$ . Polymerization of I is a chain reaction without branching. J. J. Bikerman

LA 2)

Kinetics of polymerization of vinyl compounds. II.  
Photopolymerization of allyl chloride. P. S. Shautarovitch  
and S. S. Medvedev (Acad. Sci. U.S.S.R., Moscow).  
*Zhur. Fiz. Khim.* 24, 10-20(1950); cf. *C.A.* 44, 2836.  
Allyl chloride (I) in  $\text{Et}_2\text{OAc}$  polymerized in light of 3630  
and 3130 Å, at a rate  $v$  independent of diln. ( $2.6 \times 10^{-2} M$ ) and  
proportional to light intensity  $I$ , at  $I = 0 \times 10^{-4}$  (units $^2$ )  
 $v$  was  $7.8 \times 10^{-5}$ ,  $5.4 \times 10^{-5}$ ,  $3.7 \times 10^{-5}$ , and  $2.8 \times 10^{-5}$   
mole sec. cc at  $75^\circ$ ,  $60^\circ$ ,  $45^\circ$ , and  $30^\circ$ , resp. Polymeriza-  
tion in the dark, also after illumination, was negligible.  
The mol. wt.  $M$ , detd. cryoscopically, of the final product  
was 1000-1200, 850, 870, and 410 at  $75^\circ$ ,  $60^\circ$ ,  $45^\circ$ , and  $30^\circ$ ,  
resp.; it was independent of diln. The apparent energy of  
activation was 4100-4400 cal. The active radical (II) of  
the growing chain reacts with a mol. of I forming (with  
reaction const.  $k_2$ ) a radical  $\text{CH}_2\text{:CHCH}_2$  (III) which is  
not active enough to react with I but adds to II thus in-  
terrupting the chain. This mechanism yields the equation  
 $v = ak_2k_1/2k_3k_4$ ; these consts. are for the reactions "ex-  
cited monomer + normal monomer  $\rightarrow$  2 normal monomers"  
( $k_1$ ), "excited monomer  $\rightarrow$  radical" ( $k_2$ ), and "radical +  
monomer  $\rightarrow$  dimer" ( $k_3$ ). The equation shows that  $v$  is  
independent of diln. and proportional to  $I$ . In this in-  
stance the length of the "kinetic chain" ( $\sigma$  = the no. of  
monomers involved in a chain initiated by one radical) is  
equal to that of the "mol. chain" ( $\lambda$  = the no. of mono-  
mers in the mol. of polymer); if III were as active as II,  $\sigma$   
would be much greater than  $\lambda$ . The kinetics of polymeri-  
zation depends on the relation between  $\lambda$  and  $\sigma$ .

J. J. Bikerman

MEDVEDEV, S. S.

Jul 51

USSR/Chemistry - Plastics

"Kinetics of the Polymerization of Vinyl Chloride in Solutions Under the Action of Benzoyl Peroxide," G. V. Tkachevko, P. M. Khomikovskiy, S. S. Medvedev, Moscow

"Zhur Fiz Khim" Vol XXV, No 7, pp 823-836

PA 206T24

PA 196T17

## USSR/Chemistry - Plastics

Nov 51

"Catalytic Polymerization of Unsaturated Compounds. II. Effect of the Dielectric Constant of the Medium on the Catalytic Polymerization of Styrene," A. R. Gantmakher, S. S. Medvedev, Phys. Chem Inst Ioffe L. Ya. Karpov, Moscow

"Zhur Fiz Khim" Vol. XXV, No. 11, pp 1328-1334

Ionic character of processes of styrene polymerization with  $\text{SnCl}_4$  was shown by investigation of processes in solvents with different dielec consts (i.e., higher dielec const increases reaction rate). HCl addts have different effects in different

196T17

## USSR/Chemistry - Plastics (Contd)

Nov 51

solvents, accelerating reaction in ethylchloride, dichloroethane, and o-nitrotoluene, lowering reaction rate in cyclohexane, and lowering mol wt when solvent has different dielec const than HCl) Found that reaction rate is proportional to square of concn of styrene in ethyl chloride with uniform dielec const. Proposes eq for dependence.

(CIA 47 no.17: 8489 53)

196T17

Medvedev, S. S., ed.

KONFERENTSIIA po vysokomolekuliarnym soedineniiam. 7th Moscow. Chemistry  
and physics-chemistry of polymers; report Moskva, Izd-vo Akademii nauk  
SSSR, 1952. 312 p. (53-18352)

QD281.P6K6

MEDVEDEV, S. S.

USSR/Chemistry - Elastomers; Plastics

Feb 52

"Catalytic Polymerization of Unsaturated Hydrocarbons.  
III. Catalytic Polymerization of Isoprene," A. R.  
Gartsevitch, S. S. Medvedev, Phys Chem Inst imeni  
L. Ya. Karpov, Moscow

"Zhur Fiz Khim" Vol XXVI, No 2, pp 173-179

Results on the catalytic polymerization of isoprene  
with  $\text{SnCl}_4$  in an  $\text{EtCl}$  soln agree with those obtained  
on styrene. The rate of reaction increases with  
time, because there is an autocatalytic increase of  
the number of active centers in the branched chain  
reaction. Branching of reaction chains occurs under

211545

participation of  $\text{SnCl}_4$ . In agreement with the  
proposed mechanism,  $\text{EtCl}$  inhibits acceleration of  
reaction and lowers mol wt of products. At  $-80^\circ$ ,  
the branched chain polymerization of isoprene does  
not occur even with a 100% monomer. Interraction of  
growing chains with double bonds of polymer fails  
to proceed under reduction of deg or unactn. Reduction  
of the concn of monomer results in decrease of deg  
of unactn and increase of the temp of gelation.

211545

234T25

USSR/chemistry - Elastomers, Polymerization

tion

21 Oct 52

PA "Initiation Mechanism in the Catalytic Polymerization of Unsaturated Compounds," A. P. Gantmakher, S. S. Medvedev, Corr Mem, Acad Sci USSR, T. E. Lipatova

"Dok Ak Nauk SSSR" Vol 86, No 5, pp 1109-1111

A conclusion drawn by P. H. Plesch, M. Polanyi, H. A. Skinner, A. S. Evans, and G. W. Meadows is found to be incorrect. These authors claim that in the catalytic polymerization of isobutene in the liquid state or in hexane solns with  $TiCl_4$  and  $BF_3$  catalysts at

234T25

low temps, the addn of  $H_2O$ ,  $CCl_3COOH$ , etc., is necessary in order that the reaction may proceed. This is disputed in the present work: It is shown that by raising either the temp or the dielec const of the solvent, catalytic polymerization of unsatd compds can be made to proceed in the presence of aprotic acids ( $SnCl_4$ ,  $AlCl_3$ ,  $BF_3$ ,  $TiCl_4$ , and others) without the addn of  $H_2O$ ,  $CCl_3COOH$  or other substances acting on the catalyst under formation of protonic acids.

MEDVEDEV, S. S.

234T25

MEDVEDEV, S. S.

USSR

Kinetics and mechanism of copolymerization of vinyl chloride and vinylidene chloride. A. D. Abkt., S. S. Medvedev, P. M. Klimikov, N. and E. V. Zaitseva. [1]

[L. Yu. Karlov Phys.-Chem. Inst. Moscow, 1964, No. 27, 1501-2419.77; cf. U.S. 3,327,74. The copolymerization of vinyl chloride (I) and vinylidene chloride (II) in the presence of benzoyl peroxide (III) in an oil emulsion stabilized with Na oleate at temps. from -50 to 0° was studied in a described and illustrated vacuum app. The initial mole fractions ( $f_1$ ) of I, II, and III, the reaction time ( $t$ ), and the temp. ( $\theta$ ) were varied. The yield of copolymer and the mole fractions ( $f_2$ ) of I and II in the latter are calculated and graphed as joint functions of  $f_1$ ,  $f_2$ ,  $t$ , and  $\theta$ . For any value of  $f_1$ ,  $f_2$  is greater than  $f_1$ . The III is continuously consumed, when it is used up, the reaction stops. The rate of copolymerization of I and II is less than the rate of polymerization of I or II alone. II is more reactive than I, and a small amount of I is more reactive than that of II.] J. W. Lowenberg, Jr.

MEDVEDEV, S.S.

6

USSR

V. Nature of branching reagents in the radical polymerization of dienes. A. D. Atkin, S. N. Kameyava, and S. S. Medvedev. [E. Ya. Karpov Phys. Chem. Inst., Moscow, 24, No. 2, p. 277 (1958)]. Zh. Org. Khim. 1958, 14, 2276. 2

The initial rates of copolymerization ( $r$ ) of vinyl acetate (I) with 1-pentene (II) and  $\alpha$ -pentene (III), and those of polymerization of I, II, and III separately, all in the presence of benzoyl peroxide at 60°, were studied by means of a dilatometer. The ratios of copolymers formed, as well as values of  $r$ , are calculated as functions of the initial mole fraction of I. The rate constants for copolymerization of I-II and I-III are about 2100 and 5000 l./mole sec., resp. The reaction is inhibited by pentenes, this is due to the formation of allyl-type radicals. The polymerization of 1,3-butadiene is discussed. The most probable source of this reaction is through chain transnucleation of H atoms between monomers. J. W. Loweberg, Jr.

MEDVEDEV, S. S.

USSR/Chemistry - Plastics, Polymers

11 Jan 53

"The Nature of the Branching Reaction During Radical Polymerization of Dienes,"  
A. D. Abkin, S. M. Kamenskaya, S. S. Medvedev, Corr Mem Acad Sci USSR, Sci-Res  
Physicochem Inst imeni L. Ya. Marpov

DAN SSSR, Vol 83, No 2, pp 269-271

A quant appraisal is made of the specific rates of the reaction between the  
polybutadiene radical and polybutadiene particles at the mono- and di-substituted  
double bond.

PA 25/T15

MEDEV S.S.

USSR/Physics - Physical chemistry

Card 1/1 Pub. 43 - 57/62

Author(s) Sheynker, A. P., and Medvedev, S. S.

Title Polymerization temperature and its effect on the formation of butadiene-styrene copolymers

Periodical Izv. AN SSSR. Ser. fiz. 18/6, 736-737, Nov-Dec 1954

Abstract The composition of butadiene-styrene copolymers obtained at various temperatures (-15 to + 38°C) in emulsions was investigated by means of absorption spectra (2 - 15μ). The content of various configurations of butadiene links in polymer chains was also investigated and established. Glycerin was used as the antifreeze when the polymerization was carried out at below-zero temperatures. Polymer solutions in carbon bisulfide were utilized for photographing the spectra. Results are described.

Institution The L. Ya. Karpov Phys. Chem. Inst.

Submitted \*\*\*\*\*

*MEDVEDEV, S.S.*

The mechanism of emulsion polymerization. Part V.  
Zabolotskaya, I.G., Solntseva, N.V., Minkovska, and S.G.  
Medvedev. Doklady Akad. Nauk S.S.R. R. 94, 51  
(1953). The relations are illustrated among  $\bar{M}_n$ , mol.  
wt.; no. of polymer particles; the amt. of isoprene ab-  
sorbed; time; and the  $\bar{M}_n$  diam. for the emulsion polymeriza-  
tion of isoprene (2 to 14 g./100 ml. soln.) at 60°, emul-  
sified by hexadecylpyridinium bromide with  $HgCl_2$  as initiator.

Polymerization begins only in a particular micelle in which a  
free radical or initiator mol. is present; then continues so that  
almost all the micelles participate, and the no. of polymer  
particles increases very rapidly without much change in  
particle size. Marked increase in particle size occurs only

"APPROVED FOR RELEASE: 07/12/2001 CIA-RDP86-00513R001033310001-9

particles increase very rapidly without much change in  
particle size. Marked increase in particle size occurs only  
after uncombined soap molecules disappear. P. H. R.

APPROVED FOR RELEASE: 07/12/2001 CIA-RDP86-00513R001033310001-9"

~~MEDVEDEV S.S.~~

The structure of polyacrylic esters by the method of light scattering. I. G. Soboleva, N. V. Makhotova, and S. S. Medvedev. *Izdat. Akad. Nauk S.S.R.*, 94, 251-92 (1981). Butyl acrylate (I) and polymethyl acrylate (II) were prepared polymerizing the esters at  $50^{\circ}$  in the presence of 0.01 mole/l.  $\text{Bi}_2\text{O}_3$  and at varying conversion. Under these conditions, II is nonlinear, but the branching is not great enough to influence the viscosity of the solns. The presence in I of short side chains does not alter the properties characteristic of linear polymers. — E. M. Leiserson

62

(2)

MEDVEDEV, S. S.

USSR/Physical Chemistry

Card 1/1

Authors : Kargin, V. A. Academician; Malinskiy, Yu. M., and Medvedev, S. S.  
Memb. corresp. of the Acad. of Sc. USSR.

Title : Investigation of monomolecular polyacrylate films

Periodical : Dokl. AN SSSR, 96, Ed. 2. 307 - 309, May 1954

Abstract : The chain molecules of polyacrylates (as well as many other high polymers) are oriented flatwise over an aqueous surface, whereby the carbonyl atoms of oxygen are the "anchors" binding the macromolecule with the surface of the water and the side paraffinic chains "project" into the air. A solid mono-layer of the polyacrylate has a greater thickness than a mono-layer of polymethylacrylate and a smaller specific area. During compression of the solid mono-layer takes place the ejection of individual chain links. Three references; 2 USSR, Table.

Institution : \*\*\*\*\*

Submitted : March 18, 1954

Medvedev, S. S.

USSR/ Chemistry - Conference

Card I/I Pub. 124 - 15/45

Author(s) : Medvedev, S. S., Memb. Corresp. of Acad. of Sc. USSR

Title : Conference on macromolecular chemistry in Milan and Turin

Periodical : Vest. AN SSSR 2, 72-74, Feb 1955

Abstract : An account is presented of special scientific conferences held during September 27 through October 2, 1954 in two of the largest industrial cities of northern Italy, Milan and Turin. The convention was arranged by the Commission on Macromolecular Chemistry at the International Society of Pure and Applied Chemistry and the main topics of the conference are listed.

Institution : -----

Submitted : -----

"APPROVED FOR RELEASE: 07/12/2001

CIA-RDP86-00513R001033310001-9

MEDVEDEV, S. S.

400  
22

2 May

✓ 463. Investigation of polymerization kinetics of  
isoprene in aqueous solutions of the emulsifier and  
in emulsions. A. P. Shnitnik and S. S. Medvedev.

APPROVED FOR RELEASE: 07/12/2001

CIA-RDP86-00513R001033310001-9"

Zhuravlev, Khim. 1955. 89. 400-70. Number 6.  
Abstract: 1955. 6. 702. It was desired to study the mechanism of emulsion polymerization stage by stage, and boronite was selected for study with a cation-active emulsifier and a water-soluble initiator. Polymerization does not begin until the introduction of the emulsifier. It appears that the entire sequence of polymerization takes place within the emulsifier or on the adsorption layer on polymeric particles and emulsion droplets, the part played by the latter process being small. Polymerization within the polymeric particles practically does not occur on account of the very weak concentration of the initiator in the polymeric particles. The constant amount of emulsifier means constancy of the total surface of the polymeric particles and a steady rate of polymerization. The formulas developed from these concepts agree well with test results.

✓

"APPROVED FOR RELEASE: 07/12/2001

CIA-RDP86-00513R001033310001-9

in polarization, the torque developed from  
these concepts agree well with test results.

882D22.192

67

APPROVED FOR RELEASE: 07/12/2001

CIA-RDP86-00513R001033310001-9"

7 8  
Formation of free radicals in photopolymerization and  
radiochemical polymerization processes. V. I. Krasil'nikov,  
V. A. Goryainov, V. V. Kostylev, V. V. Likhachev, V. V. Slobodchikov,  
A. V. Tsvetkov, Yu. N. Yushkevich. In this paper  
attention is given to the formation of free radicals in the  
processes of photopolymerization and radiochemical  
polymerization. The authors have made an attempt to  
analyze the radiation processes in the formation of free  
radicals. The radiation processes are considered as the  
conversion of excited monomers into biradicals which are rapidly  
transformed into monoradicals. The quantum yield is  
low, varying from 0.012 for  $\text{Mg}\text{Cl}_2$  methacrylate to 0.0001 for  
polystyrene. In the implementation of styrene, the presence of  
 $\text{CCl}_4$  increases the quantum yield. In such a case the free  
radicals are produced following the reaction between the  
monomeric excited mol. and  $\text{CCl}_4$ . James R. Oliver.

"APPROVED FOR RELEASE: 07/12/2001

CIA-RDP86-00513R001033310001-9

FM RDP  
NET

APPROVED FOR RELEASE: 07/12/2001

CIA-RDP86-00513R001033310001-9"

*MEDVEDEV, S.S.*

USSR/ Catalytic polymerization

Card 1/2              Pub. - 21/52

Authors : Gantmakher, A. R., and Medvedev, S. S. Act. Memb. of Acad. of Sc. USSR

Title : Some peculiarities of the kinetics of combined catalytic polymerization

Periodical : Dok. AN SSSR, 100/2, 275-278, Jan 11, 1955

Abstract : Investigation was made to determine the kinetics of combined and separate catalytic polymerization of isoprene-butadiene and styrene-butadiene systems. The polymerization was carried out in EtCl with SnCl<sub>4</sub> as catalyst at 0° by the dilatometric method. Results indicate that the butadiene polymerization does not take place at temperatures of from 0 to 20°; the polymerization with this less active catalyst requires much higher temperatures. Isoprene with SnCl<sub>4</sub> was observed to polymerize at temperatures ranging from 0 to -80°.

Institution : The L. I. Karpov Scientific Research Phys-Chem. Institute

Submitted : July 3, 1954

Periodical : Dok. AN SSSR, 100/2, 275-278, Jan 11, 1955

Card 2/2 Pub. 22 - 21/52

Abstract : Initial and maximum rate of polymerization were increasing after adding a relatively large amount of butadiene to the isoprene. An entirely different effect was observed during the addition of butadiene to styrene. Eight references: 2 English; 2 USA; 1 German and 3 USSR (1923-1951). Table; graph.

Medvedev, S. S.

USSR/Chemistry - Catalytic polymerization

Card 1/1 Pub. 22 - 22/49

Authors : Lipatova, T. E.; Gantmakher, A. R.; and Medvedev, S. S. Memb. Corresp.

of Acad. of Sc., USSR

Title : Catalytic copolymerization of unsaturated compounds

Periodical : Dok. AN SSSR 100/5, 925-928, Feb 11, 1955

Abstract : The kinetics of catalytic copolymerization of isoprene-styrene, isoprene-alpha-methylstyrene systems over  $\text{SnCl}_4$  catalysts was investigated to determine the copolymerization constants for these systems. The dependence of the copolymerization rate upon the composition of the basic mixture and the molecular weights of the homologous copolymers were determined. The ion mechanism of catalytic polymerization in the presence of an  $\text{SnCl}_4$  catalyst is explained. Eight references: 6 USA and 2 USSR (1944-1955). Table; graphs.

Institution : \*\*\*\*\*

Submitted : July 3, 1954

MEDVEDEV, S.S.

USSR/Chemistry

Physical Chemistry

Card : 1/1

Authors : Sheynker, A. P., and Medvedev, S. S., Member Corresp. of Acad. of Sc. USSR

Title : Investigation of the kinetics of polymerization of isoprene in aqueous emulsifier solutions and emulsions

Periodical : Dokl. AN SSSR, 97, Ed. 1, 111 - 114, July 1954

Abstract : The kinetics of isoprene polymerization was investigated in water, in N-cetylpyridine bromide emulsifier solutions and in emulsions under the effect of a water-soluble initiator ( $H_2O_2$ ) for the purpose of determining the mechanism of emulsion polymerization. The kinetic measurements in emulsifier solutions not saturated with isoprene and in emulsions were carried out by means of the dilatometric method. The results are presented in table and graphs. Four references: 2 USSR and 2 USA.

Institution : The L. Ya. Karpov Scientific-Research Physico-Chemical Institute

Submitted : March 20, 1954

Medvedev, S.S.

Effect of polymerization temperature on the structure of copolymers of butadiene with styrene. A. P. Shemtsev and S. S. Medvedev. *Doklady Akad. Nauk S.S.R.* 102, 1143-5 (1955). Infrared exam. was made of copolymers of butadiene with PhCH<sub>2</sub>CH<sub>3</sub> at -15° to 35°. Kinetic data, shown graphically, for polymerizations which were run in aq. phase with Na sulfonate emulsifier, show that rise in temp. gave higher polymer yields, while introduction of glycerol into the mixt. (for antifreeze purposes) reduced the yield of polymer somewhat. The energy of activation was estd. at 9 cal./mole. The no. of styrene units was estd. from intensity of differential infrared absorption at 700 cm.<sup>-1</sup> (2h ring), while the butadiene content was estd. from 867 and 900 bands. (For calcn. techniques, cf. Hart and Meyer, *C.A.* 43, 7822; M. *C.A.* 43, 3725; Cross, et al., *C.A.* 46, 34051). Polymers prep'd. in the absence of glycerol showed the content of trans structure increased by 17% when the temp. was raised from 0° to 45°. No polymer compn. change was observed. Unsatn. of the polymer prep'd. in the presence of glycerol was decidedly smaller than that found in specimens prep'd. in the presence of glycerol, if calcd. on the wt. of the polymer; calcd. on the basis of butadiene links, the unsatn. was the same in both cases. Products formed at -15° in the presence of glycerol had the same compn. as those formed at 20°, in respect to cis-trans components. G. M. Kosolapoff (1)

MEDVEDEV, S. S.

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Polymerization of chloroprene in presence of  $\alpha$ -polymer. A. N. Pravednikov and S. S. Medvedev [Dokl. Akad. Nauk SSSR, 1955, 105, 461-464]. Between 5 and 25% the rate of polymerization of chloroprene to vitreous  $\alpha$ -polymer is expressed by  $dW/dt = k'W$ , where  $W$  is the wt. of polymer. Strains arising in the polymerizing mass lead to rupture of polymer chains, with formation of free radicals, the no. of which ( $n$ ) is proportional to  $W$ , whence  $dn/dt = k''n$ . At temp. exceeding the vitrification point, the rate of extinction of free-radical reaction chains rises owing to lowered  $\gamma$  of the mass, and the rate of formation of active centres of initiation of chains is expressed by  $dn/dt = k'''n - k''n^2/V$ , where  $V$  is vol. of polymer. R. TRUSCOZ

M. A. YOUTZ

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MEDVEDEV, S.S. (Chkalov).

Regularities in the operator's performance [with English summary  
in insert]. Avtom.i telem. 17 no.11:985-1000 N '56. (MLRA 9:12)  
(Labor productivity)

MEDVEDEV, S.S.

Relation of seismic action to the natural vibration periods of  
structures. Trudy Geofiz.inst. no.36:80-113 '56. (MLRA 9:8)  
(Earthquakes and building)

Medvedev, S.S.

86-1-27/30

AUTHOR: Aronin, G.S., Engr Col, Docent, Candidate of Technical Sciences; and Medvedev, S.S., Engr Lt Col, Candidate of Technical Sciences.

TITLE: Estimating the Combat Capacities of Fighters (O rashchete boyevykh vozmozhnostey istrebiteley).

PERIODICAL: Vestnik Vozdushnogo Flota, 1958, Nr 1, pp. 84-86 (USSR)

ABSTRACT: Under this title appear two articles under the following subtitles: 1. "Unjustified Method" by Engr Col G.S. Aronin and 2. "To Continue the Research for a More Acceptable Method", by Engr Lt Col S.S. Medvedev. The authors discuss the article "Combat Capacities of Fighters and the Method of Determining Them" by Col R.Ya. Kudryashov and Lt Col P.G. Nikitin, which was published in the No. 8 issue of this periodical in 1957. Both, Aronin and Medvedev, raised

Card 1/2

86-1-27/30

Estimating the Combat Capacities of Fighters (Cont.)

some objections to the method suggested by Kudryashov and Nikitin. Particular attention is drawn to the inadequacy of the new concept of "determining the degree of superiority of the fighter-plane over the enemy", which is expressed by coefficient C in the final formula of the computations.

AVAILABLE: Library of Congress

Card 2/2

sov/86-58-8-13/37

AUTHOR: Medvedev, S.S., Engr Col, Candidate of Technical Sciences

TITLE: Calculation of Dynamic Characteristics of a Gunsight While Firing (Uchet dinamicheskikh kharakteristik pritsela pri strel'be)

PERIODICAL: Vestnik vozdushnogo flota, 1958, Nr 8, pp 37-39 (USSR)

ABSTRACT: The author states that a knowledge of the dynamic characteristics of a gunsight is of great importance in modern air battle, because this helps to improve the accuracy of firing and reduces the time of tracking a target. The author describes how the main component of total corrections, the lead angle, is plotted during the aiming procedure with the ASP-3 gunsight. Four graphs.

Card 1/1

MEDVEDEV, S. S., and SHEYKHER, A. F.

"Study of the Kinetics of Polymerization in Colloid Solutions of Soaps and Emulsions"  
(Issledovaniye kinetiki polimerizatsii v kolloidnykh rastvorekh myl i emul'siyakh)  
from the book Trudy of the Third All-Union Conference on Colloid Chemistry, pp. 450-457,  
Iz. AN SSSR, Moscow, 1956

{Report given at above Conference, Minsk, 21-4 Dec 53}

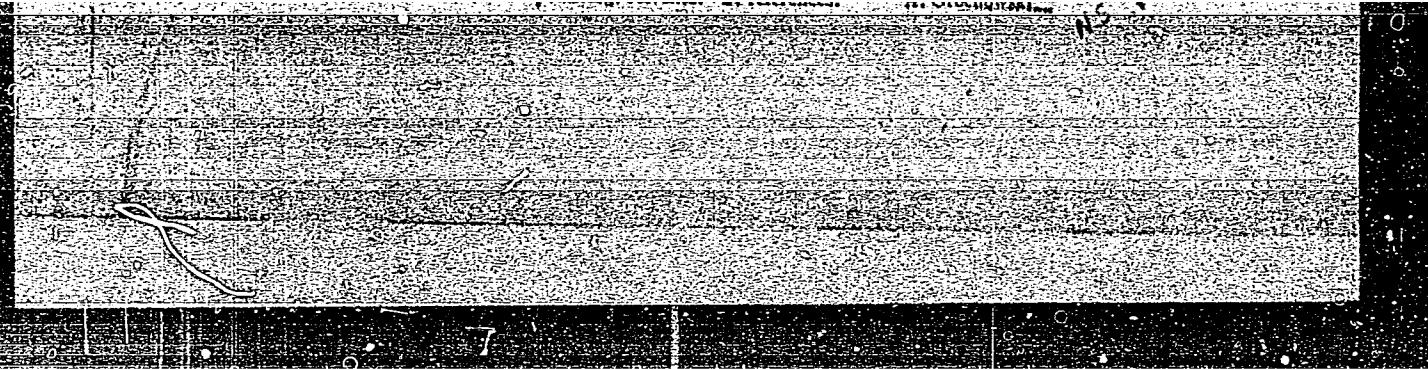
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EU

Chemical reactions in dispersed systems in connection with the mechanism of emulsion polymerization. P. M. Khomitovskii and S. S. Medvedev. *Trudy V. V. Veroyus Kons-Kravd. Khim. Akad. Nauk S.S.R., Otdel. Khim. Nauk* 1956, 440-9. Elementary reactions taking place during emulsion polymerization were discussed and several sources, mostly Russian, were quoted. Examples given are polymerization of styrene and of Me methacrylate in water and in emulsifier soins, such as Na borate. The increase of the total velocity of the reaction during the emulsion polymerization takes place not only because of the decrease in the velocity of the chain transfer.

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USSR/Chemistry of High-Molecular Substances, F

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 1110

Author: Soboleva, I. G., Makletsova, N. V., Matveyeva, A. V., and Medvedev,  
S. S.

Institution: None

Title: Investigation of the Structure of Butadiene-Styrene Copolymers

Original  
Periodical: Kolloid. zh., 1956, Vol 18, No 3, 344-349 (published with a summary  
in English)

Abstract: Osmometric (osm) and light-scattering (list) methods have been applied  
to the determination of the molecular weight M of a number of butadiene-  
styrene copolymer fractions, prepared by carrying out polymerization  
until varying degrees of conversion were achieved, as well as of some  
unfractionated polymers; the dissymmetry factor and the intrinsic vis-  
cosity were also determined. The large differences between M (osm) and  
M (list) which were observed point to the presence of relatively large  
amounts of very large particles in the butadiene-styrene copolymer

Card 1/2

USSR/Chemistry of High-Molecular Substances, F

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 1110

Abstract: solution. The influence of these particles can be detected only by statistical averaging. The presence of such particles is also indicated by the large values of the dissymmetry factor and the turbidity factor. The authors assume that the macroparticles present in solution form the seeds of extended layers. The hypothesis postulating the formation of large molecules with extended chains during the polymerization of styrene with butadiene is also confirmed by the low rate of increase in the assymmetry of light dispersion and the reduction in intrinsic viscosity with increasing molecular weight. It is shown that the heterogeneity of the fractions and chain length of the copolymer molecules increase with conversion and reaction temperature.

Card 2/2

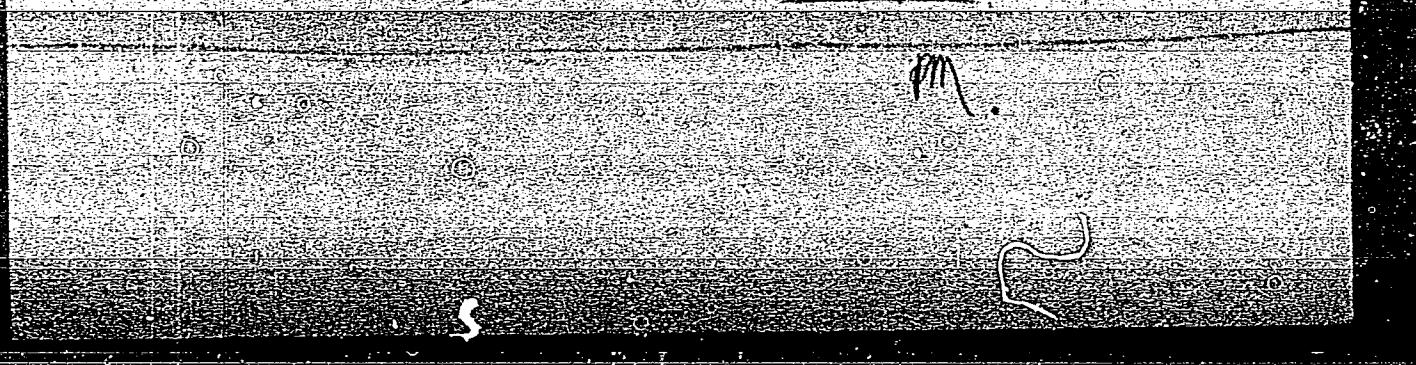
Medvedev, S.S.

✓ Study of the mechanism of emulsion polymerization  
B. V. Zabolotskaya, I. G. Sosulin, N. V. Matuzanova, and  
S. S. Medvedev (J. Ya. Karpe Inst. Phys. Chem., Moscow),  
*Zh. fiz. khim.* 18, 420-8 (1950); cf. *C.A.* 45, 16201b.

An eq. soln. of *N*-cetylpyridinium bromide (I) and  $H_2O$   
(0.45%) was continually irradiated with isoprene (II) vapor at  
20°. Except during a 1st period (of 5 min.), the rate of the  
decrease of II by the eq. phase (i.e. polymerization) was const.  
In the next reaction, it was greater when the concn. of I  
was greater (8% instead of 2.5%). The total area of the  
latex globules in 1 cc. changed little during the reaction;  
it was about  $4 \times 10^4$  sq. cm. in 8% I and  $3.2 \times 10^4$  sq. cm. in 2.5% I.  
It thus the reaction occurred on the surface of the globules.

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MEDVEDEV S.

Kinetics and mechanism for polymerization processes based on organic radical polyvalence. I. Kinetic and mechanisms for initiating polymerization processes in aqueous solutions of alkyl compounds. T. M. Grigorev and V. N. Medvedev. *Vysokomol. Soedin.*, 1970, v. 12, p. 1056-1063. The kinetics of the polymerization of methyl vinyl ketone and vinyl acetate (I) in the presence of the hydroperoxide of cumene ( $\text{C}_9\text{H}_{10}\text{O}_2\text{MgOOH}$ ) (II) was studied by the dilatometric method in the temp. range 30-75°. Kinetic equations were derived on the basis of the following 2 mechanisms for the formation of the initial active centers: (a) unimolecular decompn. of II and

*D.M.E.W.*

GRITSENKO, T.M.; MEDVEDEV, S.S.

Kinetics and mechanism of polymerization initiated by redox systems. Part 2. Polymerization in aqueous solution of methacrylic acid and acrylonitrile in the presence of certain redox systems [with English summary in insert]. Zhur.fiz.khim. 30 no.7:1513-1520 J1 '56. (MLRA 9:11)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova, Moskva.  
(Methacrylic acid) (Acrylonitrile) (Polymerization)

MEDVEDEV, S. S.

✓ The homogeneous cationic polymerization of isoprene  
with compounds of the same active polymerization in  
presence of styrene / I. E. Linnikova, A. R. Samokhina,  
and N. S. Medvedev (L. V. Kurnov Phys.-Chem. Inst.,  
Moscow). Zhur. Fiz. Khim. 30, 1762-3 (1956). — The rate  
of polymerization was studied in relation to the compn. of  
the starting mixt. The mol. wt. and the compn. of the  
polymers were detd. The data show that 3 components  
participate in the polymerization: isoprene, styrene, and the  
copolymer. The data on the compn. of the copolymer show

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water is enriched in its isoprene content. [Signature]

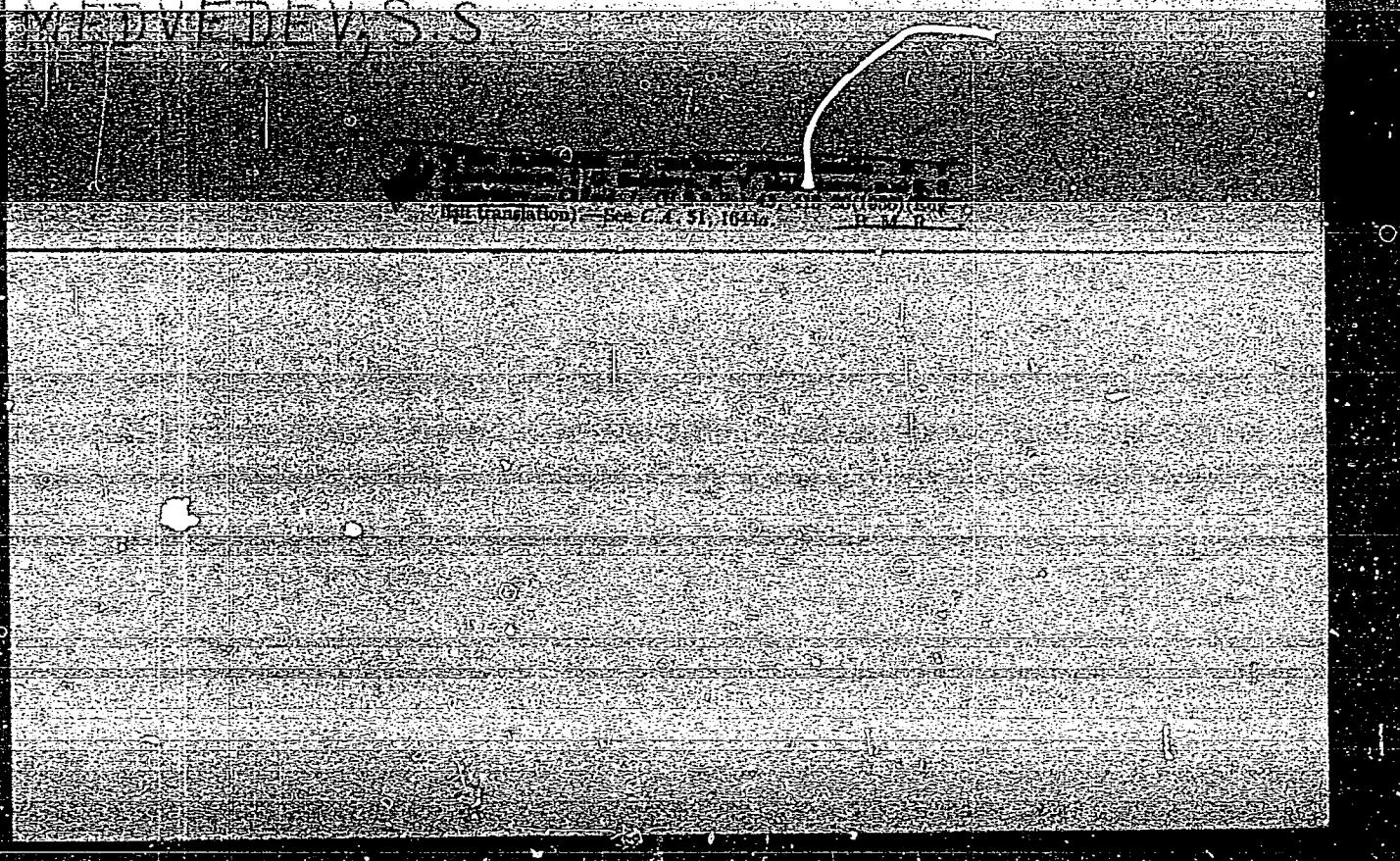
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Medvedev, S. S.

USSR/ Chemistry - Physical chemistry

Card 1/1 Pub. 22 - 34/54

Authors : Soboleva, I. G.; Makletsova, N. V.; and Medvedev, S. S., Memb. Corr.:  
Acad. of Sc., USSR

Title : Formation of polymers in solutions in presence of a precipitating agent

Periodical : Dok. AN SSSR 106/2, 303-306, Jan 11, 1956

Abstract : Linear polystyrene and butadiene-styrene copolymers having a different degree of branching were investigating to determine the structure of polymers formed in solutions in the presence of a settling agent. Nephelometric molecule dimension measurements were made in a pure toluene solution of polystyrene and in solutions with different settling agent admixtures. The minimum molecule dimension observed near the point of settling was found to be the parameter characterizing the structure of the molecular polymer chain and the branching properties of polymers. Six references: 3 USSR, 1 Eng., 1 USA and 1 French (1950-1954). Tables; graphs.

Institution : Scient. Res. Physicochemical Inst. im. L. Ya. Karpov

Submitted : April 1, 1955

MEDVEDEV, S.S.

Investigation of copolymerization of hexadecyl and methyl acrylates in  $\text{C}_6$  (benzene) solution. S. N. Kamenskaya, A. D. Adsin, and S. S. Medvedev. Doklady Akad. Nauk S.S.R. 106, 855 (1956). Z. R. 45, 3227. — The relative reactivity of polymerization of 2 chemically similar monomers and their copolymerization was studied on the basis of the results reported before (66, etc.). Me acrylate was purified by washing, drying, and distn. at 38–0° and 155 mm. Hg. Ether distn. from the monomer was used in its polymerization, doing away with the induction period. Hexadecyl acrylate was synthesized from hexadecanol and Me acrylate in the presence of  $\beta$ -toluenesulfonic acid. The ester was distd. in  $\text{C}_6$  in the presence of metallic Cu, and the 155–00° fraction at 1.8 mm. Hg, m.p. 24°,  $n_{D}^{20} = 1.4599$ ,  $d_{4}^{20} = 0.859$ , was collected. Pure  $\text{Bz}_2\text{O}$  was used as the reaction initiator. For copolymerization, a toluene soln. with the monomer concn. of 1.5 n<sup>o</sup> (es/l.) was used. The polymerization rate was observed dilatometrically, at 50  $\pm$  0.05°. The hexadecyl acrylate polymerization rate was found to be 2.8 times greater than of Me acrylate, and this rate was found to be the same at lower concns. of monomers. The copolymerization rate was calcd. by using the previously derived formula, which involved the use of the individual polymerization rates of the monomers, and the coeff.  $\lambda$  which characterizes the ratio of the ratio of the constants of the individual monomers polymerization initiation. The value of  $\lambda$  was found to > 0 from the kinetic data, and nearly the same value from the av. of polymerization. By assuming the value for the Me acrylate chain growth rate  $K_{A,A} = 10^{6.78 \pm 0.07}$  (Matheson, et al., C.A. 46, 1852), the values for  $K_{A,A} = 1658$ ;  $K_{B,B} = 1507$ ;  $K_{A,B} = 1731$ ; and  $K_{B,A} = 1256$ .

M. A. YUDZ  
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**Termination of catalyst by polymer.** A system of uninitiated polymerization may be considered as consisting of two parts: (1) the initiation of polymerization, which is the formation of polymer chains; and (2) the termination of polymerization, which is the breaking of reaction chains, for which the velocity constants are  $k_1$  and  $k_2$ , respectively. The rate of the velocity of polymerization is given by the equation:

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*1-μm*

Investigation of the  $\alpha$ -polymerization mechanism of chloroprene by the tagged atom method. A. N. Pravednikov and S. S. Medvedev. *Doklady Akad. Nauk S.S.R.* 109, 579-581 (1956). The polymerization process which results in the rupture of C-C bond polymer chains was studied experimentally. To accomplish it C<sup>14</sup>-contg. chloroprene was synthesized, in which the  $\alpha$ -polymer nucleus was produced in the usual way, and the radioactivity distribution in the polymer was investigated. If a polymerization process without any C-C bond rupture would cause only the polymer outer part to be radioactive; if there is a rupture the whole polymer would be radioactive. These results, and the results given earlier (*C.A.* 50, 4543) permit the description of the chloroprene polymerization process as proceeding by an anion mechanism and also with a  $\omega$ -polymer formation by radical formation through the rupture of polymer mols.

W. M. Sternberg

R.M. *and*  
R.M.J.

MEDVEDEV, S.S.

Category: USSR/Chemistry of High-Molecular Substances

F.

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 30897

Author : Gritsenko T.M., Medvedev S.S..

Inst : Academy of Sciences USSR

Title : Kinetics of Polymerization of Acrylic Acid and Methacryl nitril  
in Water Solution in the Presence of Cumene Hydroperoxide

Orig Pub: Dokl. AN SSSR, 1956, 110, No 2, 235-237

Abstract: Study of the kinetics of polymerization of acrylic acid (I) and nitril of methacrylic acid (II) in aqueous solutions in the presence of cumene hydroperoxide (III) at 30-70°. Summative energy of activation of I and II, respectively, is of 9.0 and 20.2 kcal/mole. Polymerization of II occurs with acceleration with lapse of time, which the authors attribute to the capacity of II-polymer to extract II and III from the solution. Order of reaction of the monomer is 3/2 in both instances. Dependence of initial rate of polymerization of I and II on the concentration of III, are analogous to those previously deter-

Card : 1/2

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MEDVEDEV, S. S., and PRAVEDNIKOV, A. N.

"Kinetics and mechanism of chloroprene polymerization," a paper presented at the 9th Congress on the Chemistry and Physics of High Polymers, 28 Jan-2 Feb 57, Moscow, Karpov Inst.

B-3,084,395

MEDVEDEV, S. S., and GANTMAKHER, A. A.

"Kinetics of copolymerization," a paper presented at the 9th Congress on the Chemistry and Physics of High Polymers, 26 Jan-2 Feb 57, Moscow, Karpov Inst.

B-3,004,395

MEDVEDEV, S. G., and GRIZENKO, T. M.

"Initiation of emulsion copolymerization with cumylhydroperoxide," a  
paper presented at the 9th Congress on the Chemistry and Physics of High  
Polymers, 28 Jan-2 Feb 57, Moscow, Karpov Inst.

B-3,084,395

MEDVEDEV, S. S., and KHONYAKOVSKII, P. M.

"Activation energy in emulsion polymerization," a paper presented at  
the 9th Congress on the Chemistry and Physics of High Polymers, 28 Jan-2 Feb  
57, Moscow, Karpov Inst.

B-3,084,395

MEDVEDEV, S. S., and SABOLOTSKAYA, E. V.

"The role of absorbed layers in emulsion-polymerization," a paper presented at the 9th Congress on the Chemistry and Physics of High Polymers, 2<sup>nd</sup> Jan-2 Feb 57, Moscow, Karpov Inst.

B-3,084,395

MEDVEDEV, S. S.

"Radiation polymerization," a paper submitted at the International Conference on Radioisotopes in Scientific Research, Paris, 9-20 Sep ,7.

MEDVEDEV, S. S. Prof.

"Mechanism of Initiation," Section II, paper submitted at the  
International Symposium on Macromolecular Chemistry, Prague, 9-15 Sep 1957

C-3,800,271

MEDVEDEV S.S.

(card 2)

AUTHOR: None Given

3-9-19/31

TITLE: Inter-vuz Scientific Conferences (Mezhvuzovskiye nauchnyye konferentsii)

PERIODICAL: Vestnik Vysshey Shkoly, 1957, # 9, pp 73 - 76 (USSR)

ABSTRACT: In January 1957, the Second All-Union Conference on Photosynthesis took place, organized by the Institute of Plant Physiology of the Academy of Sciences, USSR, and by the Faculty of Soil-Biology of the Moskva University. About 700 representatives of 130 scientific-research institutes, vuzes and ministries were present. The introductory report was made by Academician A.L. Kursanov who described the development of photosynthesis during the last ten years and invited the scientists to concentrate their work on the application of radioactive and stable isotopes. Nearly 100 reports were read: 13 on photochemistry, 9 on the investigation of chloroplast structure, 19 on the investigation of pigments, 9 on the photosynthesis of water plants, bacteria, etc.

Reports on the results reached in the field of photosynthesis were made by: Doctor G. Polster from the German Democratic Republic, Professor N. Seledzhanu from the Rumanian People's Republic, Professor K. Popov from the Bulgarian People's Republic. Finally the Conference stated the great role of Soviet scientists in the development of photosynthesis and gave some defi-

Card 1/7

Inter-vuz Scientific Conferences

3-9-19/31

ciencies in the research organization, in particular, the insufficient participation of biologists in the solution of the problem in question.

The Ninth Conference on High-molecular Combinations took place from 28 January to 1 February. It was organized by the USSR Academy of Sciences and the MGU and concentrated on general matters of polymeric chemistry and physics. About 1500 scientists were present from 172 organizations and 37 towns of the Soviet Union, the representatives of 42 vuzes and 17 foreign scientists from China, East Germany, Poland, Rumania, Czechoslovakia, Yugoslavia, the German Federal Republic and Israel.

The introductory speech was made by Academician V.A. Kargin, who described the present state of science relating to polymers, and invited the scientists to concentrate their work on new methods of obtaining polymers, and new classes of high-molecular substances. In the section of polymeric synthesis 43 papers were read. The author enumerates the following reports: Academician A.N. Nesmeyanov on the reaction of ethylene polymerization and carbon tetrachloride.

S.S. Medvedev, Member-Correspondent of the USSR Academy of Sciences, on the kinetics of various types of polymerization.

Professor B. A. Dolgoploska (Leningrad) on the initiation of radical polymerization.

Card 2 / 7